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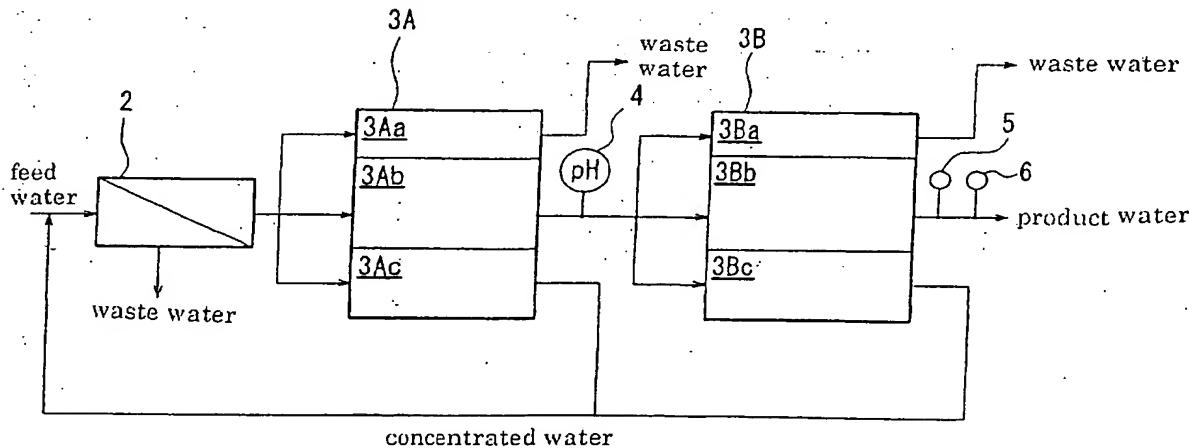
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(54) Electrodeionization apparatus and pure water producing apparatus

(57) The electrodeionization apparatus improves the removal rate of weakly - ionized species including silica and boron, and which species including silica and boron, and is useful for a primary pure water system and a reclaim system. The apparatus for producing purified water produces the product water of high quality including the resistivity of equal to or more than 18.0 MΩ · cm can be provided. The electrodeionization apparatus 3A has a plurality of cation exchange membrane and plurality of anion exchange membrane alternately arranged

between electrodes in such a manner as to alternately form diluting compartments and concentrating compartments. The diluting compartments are filled with an ion exchanger. The product water having pH exceeding pH of the feed water by 1.0 or more when the feed water having pH of equal to or less than 8.5 is treated without adding alkaline agents. The apparatus for producing purified water has plural electrodeionization apparatuses 3A, 3B connected each other so that the feed water flows through the electrodeionization apparatuses.

Fig. 1



Description

[0001] The present invention relates to an electrodeionization apparatus used for producing deionized water in various of fields including semiconductor manufacturing, liquid crystal display manufacturing, pharmaceutical manufacturing, food processing, electric power generation, private device, research establishments and the like, particularly to an electrodeionization apparatus. More particularly the present invention relates to the electrodeionization apparatus which removes weakly - ionized species electrolytes including silica and boron at a high rate, and is suitable to be employed by a primary pure water system and a reclaim system of pure water producing apparatus.

[0002] Further more, the present invention relates to an apparatus for producing purified water which employs the electrodeionization apparatus of the present invention so that the apparatus provides the product water of high quality having resistivity of more than $18.0\text{M}\Omega \cdot \text{cm}$.

[0003] The electrodeionization apparatus used for producing the deionized water is employed in various of fields including the semiconductor manufacturing plants, the liquid crystal display manufacturing plants, the pharmaceutical manufacturing industry, the food processing industry, the electric power industry and the like, etc., the private devices, and the research establishments.

[0004] Fig.3 shows an electrodeionization apparatus disclosed in JPH4 - 72567B, JP2751090, and JP2699256 in which a plurality of anion exchange membranes 13 and a plurality of cation exchange membranes 14 are alternately arranged between electrodes (anode 11, cathode 12) in such a manner as to alternately form concentrating compartments 15 and diluting compartments 16, and the diluting compartments 16 are filled with anion exchangers and cation exchangers comprising ion exchange resins, ion exchange fibers or graft exchangers in mixed or multi-layered form. In Fig.3, the sign 17 denotes an anodic compartment and the sign 18 denotes a cathodic compartment.

[0005] In the electrodeionization apparatus, H^+ ions and OH^- ions are formed by dissociation of the water to continuously regenerate the ion exchangers filled in the diluting compartments so that the electrodeionization apparatus can efficiently deionize the water.

[0006] Fig. 12 is an exploded view showing the structure of the electrodeionization apparatus.

[0007] The electrodeionization apparatus includes a cathode end plate 101, a cathode 102 extending along the end plate 101, a cathode spacer 103 extending along the outer periphery of the cathode 102 which are superposed in this order. Further, a cation-exchange membrane 104, a frame 105 for defining a diluting compartment, an anion-exchange membrane 106, and a frame 107 for defining a concentrating compartment are superposed on the cathode spacer 103 in this order. The cation-exchange membrane 104, the frame 105 for defining a diluting compartment, the anion-exchange membrane 104, the frame 107 for defining a concentrating compartment compose one unit. The apparatus is composed of a plurality of such units superposed together. That is, membranes 104, frames 105, membranes 106, and frames 107 are repeatedly superposed one unit over the other unit. An anode 109 is superposed between the last anion-exchange membrane 106 and an anode spacer 108. An anode end plate 110 is superposed on the anodic electrode 109. The apparatus is tightened by bolts or the like.

[0008] The space defined by the inner surface of the frame 105 is the diluting compartment in which an ion exchanger 105R such as ion-exchange resin is filled. The space defined by the inner surface of the frame 107 is the concentrating compartment in which a spacer including a mesh spacer is disposed.

[0009] A direct electric current is supplied to pass between the anode 109 and the cathode 102, raw water to be treated is fed to the diluting compartment through a raw water inlet line 111, and feed water is fed to the concentrating compartment 108 through a concentrate inlet line 112. The raw water fed to the diluting compartment flows through a layer filled with the ion-exchange resin whereby impurity ion in the raw water is removed so as to make the raw water to deionized water which flows out through a deionized water outlet line 113.

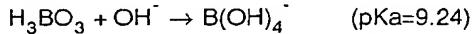
[0010] The impurity ions permeate the membranes 104, 106, the concentrated water in the concentrating compartment flows out through a concentrate outlet line 114. Electrode water is passed within electrode compartments through introducing lines 115, 116 and discharging lines 117, 118, respectively.

[0011] An electrodeionization apparatus in which a diluting compartment is provided with vertical partition ribs for dividing the diluting compartment into cells being long in the vertical direction is disclosed in JP4-72567B. According to this electrodeionization apparatus having the diluting compartment divided into long cells by ribs in which ion-exchange resins are filled respectively, the channelizing phenomenon where the flow of water from the inlet to the outlet of the diluting compartment is partially one-sided is prevented and the compression and the ion-exchange resins in the diluting compartment is prevented from being compressed or moved..

[0012] In the electrodeionization apparatus of JP4-72567B, the number of the cells is limited because the cells are formed by dividing the diluting compartment in the vertical direction. That is a large number of cells can not be formed in the apparatus. Further, the flow of the water in a lateral direction is blocked by the ribs, so that the contact efficiency between the water and the ion-exchange resins is poor. In addition, the ion-exchange resins are compressed at lower portions of the cells so that the cells have a vacancy at upper portions thereof, whereby the rate of filling the ion-exchange resins tends to be poor.

[0013] Fig.4 is a system diagram showing a conventional apparatus for producing purified water provided with the electrodeionization apparatus in which raw water such as the city water is treated in an activated carbon treating device 1, a reverse osmosis membrane treating device 2, and an electrodeionization apparatus 3.

[0014] To remove weakly - ionized species electrolytes including carbon dioxide gas (CO_2), silica, boron and the like in an electrodeionization apparatus, it is required to ionize these species and form ions as follows in diluting compartments:



[0015] Even the conventional electrodeionization apparatus can completely remove weakly - ionized species having low dissociation constant (pK_a) such as CO_2 by increasing the applied voltage to dissociate water. However the conventional electrodeionization apparatus scarcely removes weakly - ionized species having high dissociation constant such as silica and boron on the order 60 to 90% even when the applied voltage is increased.

[0016] In order to solve above problems, the following have been proposed.

- I. To fill diluting compartments with multi - layered ion exchangers composed of an anion exchange layer and a cation exchange layer so as to make the water alkaline in the anion exchange layer (as disclosed in JP - H471624A).
- II. To adjust pH of feed water in a range of 9.5 to 11.5 to be fed into the electrodeionization apparatus (as disclosed in USP 4,298,442).
- III. To provide the conventional electrodeionization apparatuses at two or more stages. To provide RO apparatuses at two or more stages to remove silica before the electrodeionization apparatus.

[0017] In the above case I, the diluting compartments filled with multi-layered ion exchangers can not lower the concentration of silica to less than 0.1 ppb as required in the fields of the semiconductor manufacturing and the like.

[0018] In the above case II, although the removal rate of silica is increased by 5 to 10%, it requires a device for adding agents including caustic soda to control pH and to provide a softening device to completely remove the hardness including Ca^{2+} and Mg^{2+} from the feed water, whereby increasing equipment costs.

[0019] In the aforementioned case III, an electrodeionization apparatus of non-regenerative mixed bed type is necessary after the electrodeionization apparatus because the water treated by the electrodeionization apparatus includes silica and boron of 0.5 to 1.0ppb or more.

[0020] Generally, when the electrodeionization apparatus is applied with the electrical current exceeding the critical current density to deionize, OH^- and H^+ are formed by water dissociation as described above to carry the electric charge. H^+ ion has mobility of $349.7 \text{ cm}^2\Omega^{-1}\text{eq}^{-1}$, which is very large in comparison with that of the other ions (30 to $70 \text{ cm}^2\Omega^{-1}\text{eq}^{-1}$, ref.; Manual of Chemistry published by Japanese Chemical Society). Therefore, particularly when the diluting compartment has a large thickness W , the difference of the mobilities between H^+ and OH^- is increased so that H^+ tends to be quickly discharged to the concentrating compartments and OH^- tends to remain in the diluting compartment. Furthermore, Na^+ and K^+ also tend to remain in the diluting compartments because these are monovalent and H^+ ion carries the electrons, while the multi-valent cations and anions including Ca^{2+} , Mg^{2+} , are discharged to the concentrating compartments with relative ease. As the result, the product water tends to include monovalent alkali such as NaOH and KOH so that the product water (deionized water) becomes alkaline.

[0021] Conversely, the concentrated water becomes acidic by the same reason.

[0022] It is an aim of the present invention to provide an electrodeionization apparatus which overcomes the aforementioned problems so that the electrodeionization apparatus is free of scale and is exceedingly improved in the removal rate of the weakly - ionized species including silica, boron and the like without adding agents such as the caustic soda. Further, it is also an object to provide an apparatus for producing purified water employing the electrodeionization apparatus.

[0023] The electrodeionization apparatus of the present invention has an anode, a cathode, concentrating compartments, and diluting compartments which are formed by arranging a plurality of anion exchange membranes and cation exchange membranes between the anode and the cathode, ion exchangers filled in the diluting compartments. The electrodeionization apparatus can produce the product water having pH higher than pH of the feed water by 1.0 or

more when the feed water having pH of equal to or less than 8.5 is treated without adding alkaline agent.

[0024] The electrodeionization apparatus of the present invention efficiently removes the weakly - ionized species including silica, boron from the feed water.

[0025] The apparatus for producing purified water of the present invention is provided with plural stages of the electrodeionization apparatuses through which the feed water flows in order. The foremost electrodeionization apparatus is the electrodeionization apparatus of present invention.

[0026] The foremost electrodeionization apparatus removes a part of carbon dioxide gas, silica, boron and the hardness from the feed water. The water treated in the foremost electrodeionization apparatus has the same in conductivity as the feed water and higher pH than the feed water.

[0027] The water treated by the foremost apparatus is then treated by conventional electrodeionization apparatus to remove the residual silica, boron and the other ions.

[0028] When the diluting compartments has a thickness exceeding the range of 1.26 to 6.35 mm as disclosed in JP H4 - 72567B and is filled with either the anion exchanger alone or the anion exchanger mixed with the cation exchanger, the electrodeionization apparatus behaves specifically. That is, when the water including a small amount of alkaline metal ion or alkaline earth metal ion which are taken out of a reverse osmosis apparatus (RO apparatus) flows through the electrodeionization apparatus, the carbon dioxide gas (CO_2) and the anion in the water are removed, besides about 90% of silica and boron are removed.

[0029] While the hardness including Ca^{2+} and Mg^{2+} is also removed, the monovalent cations including Na^+ and K^+ have difficulty in being removed and the alkalis such as NaOH and KOH which have high molar conductivity leak into the treated water so that the treated water tends to be increased in pH and slightly in conductivity.

[0030] The cause of aforementioned behavior of the electrodeionization apparatus has not been clear in detail, but supposed as follows. That is, when the electrodeionization apparatus is applied with the electrical current in excess of critical current density to deionize, OH^- and H^+ are formed by water dissociation as described above to carry the electric charge. H^+ ion has mobility of $349.7 \text{ cm}^2\Omega^{-1}\text{eq}^{-1}$, which is very large in comparison with that of the other ions (30 to $70 \text{ cm}^2\Omega^{-1}\text{eq}^{-1}$, ref ; Manual of Chemistry published by Japanese Chemical Society). Therefore, particularly when as the thickness W of the diluting compartment increases, the difference of the mobilities between H^+ and OH^- increases so that H^+ tends to be unilaterally discharged to the concentrating compartments and OH^- tends to remain in the diluting compartment. Furthermore, Na^+ and K^+ also tend to remain in the diluting compartments because H^+ ion carries the electrical charge, while the multi - valent cations and anions including Ca^{2+} , Mg^{2+} are discharged to the concentrating compartments with relative ease. As the result, the product water tends to include monovalent alkali such as NaOH and KOH so that the product water is increased in pH.

[0031] By the same reason, the concentrated water becomes acidic because of the tendency of OH^- to remain in the diluting compartment and the tendency of H^+ to be discharged from the concentrating compartment. Therefore, the electrodeionization apparatus is free of scale even when the matters such as Ca^{2+} and Mg^{2+} are concentrated at high concentration.

[0032] The electrodeionization apparatus of the present invention may be provided with a cation exchange membrane between the anode and the anion exchange membrane of the diluting compartments nearest to the anode, so that the concentrating compartments is formed between the cation exchange membrane and the diluting compartment nearest to the anode, and the anodic compartment is formed between the cation exchange membrane and the anode.

[0033] In the electrodeionization apparatus, the cation concentration in the cathodic compartment is high and the electric resistance between the electrodes is low, whereby the voltage applied to cells is decreased. To prevent formation of scale in the cathodic compartments, the electrodric water fed into the cathodic compartment is decreased in pH (or, the electrodric water is made acidic). For this purpose the thickness of the diluting compartment is increased to decrease pH of the water which flows out from the concentrating compartments and then flows into the cathodic compartment as the elecrtrode water.

[0034] The electrodeionization apparatus of the present invention is useful for a foremost electrodeionization apparatus of the apparatus for producing purified water in which two or more electrodeionization apparatuses are connected in series so as to make treatment of the feed water at plural stages. When feed water having conductivity of $10 \mu\text{S}/\text{cm}$ and including silica 200ppb and boron of 20ppb flows through the first electrodeionization apparatus of the present invention and then flows through the second conventional electrodeionization apparatus, the water flowing out from the second electrodeionization apparatus has electrical resistivity of equal to or more than $18 \text{ M}\Omega \cdot \text{cm}$ and includes silica and boron of equal to or less than 0.1ppb as like as the theoretical pure water. Since the preceding first electrodeionization apparatus removes the hardness such as Ca^{2+} and Mg^{2+} , the succeeding second electrodeionization apparatus is free of scale and has the water recovery of equal to or more than 95%. The concentrating compartment of the preceding first electrodeionization apparatus produces the acidic water and the concentrating compartment of the succeeding electrodeionization apparatus produces the alkaline water. These acidic water and alkaline water may be mixed together and be fed back to the preceding RO apparatus.

[0035] The electrodeionization apparatus of the present invention may be provided with thick cells having a thickness

of equal to or more than 7 mm and thin cells having a thickness of less than 7 mm as shown in Fig.7 and Fig.8 so that the water flows through from the thick diluting compartment to the thin cell in series.

[0036] Embodiments of the present invention will now be described by way of example only, with reference to the accompanying drawings, in which:-

5 Fig. 1 is a system diagram of an electrodeionization apparatus and an apparatus for producing purified water of the present invention according to an embodiment;

10 Fig. 2 is a flow diagram of an apparatus for producing purified water employed in Example 6.

Fig. 3 is a cross - sectional view showing a structure of a conventional electrodeionization apparatus.

15 Fig. 4 is a system diagram of a conventional apparatus for producing pure.

Fig. 5 is a graph showing the interrelationship between the applied voltage and pH of the product water observed in Example 1.

Fig. 6 is a graph showing the measurements of the resistivity and pH of the product water measured in Examples 2 to 5 and Comparative Examples 2 and 3.

20 Fig. 7 is a cross-sectional view of an electrodeionization apparatus of the present invention according to another embodiment.

Fig. 8 is a cross-sectional view of an electrodeionization apparatus of the present invention according to the other embodiment.

25 Fig. 9 is an exploded perspective view of a diluting compartments according to the other embodiments.

Fig. 10 is a front view showing a partition member under situation where the water flows along the partition member.

Fig. 11 is a front view showing an example of the partition member.

Fig. 12 is an exploded perspective view of a conventional electrodeionization apparatus.

30 Fig. 13 is a flow diagram of an apparatus for producing purified water employed in Example 7.

Fig. 14 is a graph showing interrelationship between the electrical resistance and the conductivity of the concentrated water.

Fig. 15 is a diagram showing interrelationship between the concentration of Na^+ included in the feed water to be fed into a preceding electrodeionization apparatus and pH of the product water treated by the preceding electrodeionization apparatus.

35 [0037] Hereinafter, a preferable embodiments of an electrodeionization apparatus of the present invention will be described in detail.

[0038] The electrodeionization apparatus of the present invention is so constituted that the electrodeionization apparatus can produce the product water having pH higher than that of the feed water by 1.0 or more, preferably by about 1.3 to 3.0 when the feed water has pH of equal to or less than 8.5 without adding alkaline agents.

40 [0039] The electrodeionization apparatus of the present invention efficiently removes the weakly - ionized species including silica and, boron, and the hardness by increasing pH of the water in the electrodeionization apparatus.

[0040] The electrodeionization apparatus of the present invention is preferable to employ the following constitutions i) and ii):

45 i) The diluting compartment of the electrodeionization apparatus is preferable to have a thickness of equal to or more than 7mm, and more preferably 8 to 30mm. The thickness of the diluting compartments is the thickness W of the diluting compartment 16 arranged between an anode 11 and cathode 12 as shown Fig.3.

ii) The ion exchanger filled in the diluting compartments is most preferably the mixture of the anion exchanger and the cation exchanger. When applied with high voltage, the ion exchanger may be the anion exchanger alone. Some of the diluting compartments may be filled with the mixture of the ion exchangers, and the others may be filled with the anion exchanger alone.

50 [0041] The electrodeionization apparatus wherein a certain zone in the diluting compartment is filled with the cation exchanger and the other zone in the diluting compartment is filled with the cation exchanger is unpreferably increased in resistivity of the product water and makes pH thereof neutral even when the thickness of the diluting compartment is more than 7mm. This is because the monovalent cation including sodium ion is removed by the cation exchanger.

[0042] The ion exchangers may be filled in the concentrating compartments in the first, second or later electrodeionization apparatus, whereby the voltage applied to the cells may be decreased so that the electric power consumption decreases.

55 [0043] The treatment made under conditions where the concentrating compartments are filled with the ion exchangers and the cells are applied with the voltage at 3 to 6 V per cell is almost the same as that made under conditions where the concentrating compartments are not filled with any ion exchangers and cells are applied with the voltage at 15 V per cell.

[0044] The ion exchangers may be the ion exchange resin in the form of beads or fibers, the graft polymerized exchanger in which exchanging groups are introduced into fibers or nonwoven sheet by graft polymerization, or the like.

[0045] For the purpose of providing the product water of good quality, the ion exchanger is preferable to be in the form of the beads having uniform size. The bead-shaped ion exchange resin represents that 90% of the beads fall within 10% of the average bead diameter and the relative average diameter between the anion exchange resin and the cation exchange resin is at least 0.8.

[0046] It is most preferable to operate the electrodeionization apparatus employing aforementioned constitutions i) and ii) in the manner as follows.

[0047] The cells of the diluting compartments are applied with the voltage at 1 to 50 V per cell, preferably at 6 to 50 V per cell, most preferably at 10 to 30 V per cell. The water flows at a space velocity (SV) of 30 to 150 per hour, preferably at SV of 50 to 100 per hour. When the applied voltage is too low or when SV is too high, monovalent anions including chloride ion, silica and boron leak into the product water. Conversely, when the applied voltage is too high or when SV is too low, the monovalent cations are too much removed.

[0048] When pH is equal to or more than 9.0 in the diluting compartment of the electrodeionization apparatus, silica and boron are easily removed.

[0049] The diluting compartments having uneven cells can make pH equal to or more than 9 in the diluting compartments. Specifically, the rate of the thickness of the cell near the outlet to the maximum thickness of the cell is equal to or less than 0.6.

[0050] While the ion exchange membrane employed in the present invention may be either homogeneous or heterogeneous, the rate of leakage of Na^+ of the heterogeneous membrane exceeds that of the homogeneous membrane, so that the product water is increased in pH. Therefore, the cation membrane is preferable to be heterogeneous. The anion membrane is preferable to be homogeneous so as to maintain the removing rate of silica and boron.

[0051] When the ratio of electrical resistance of the anion exchange membrane to that of the cation exchange membrane is equal to or less than 0.8, Na^+ is easily removed.

[0052] Especially when the electrodeionization apparatus having aforementioned constitutions in which the diluting compartments having a thickness of 10 to 20 mm is filled with the mixture of the anion exchange resin and the cation exchange resin, the water flows at SV of 50 to 100 per hour and the applied voltage is taken as 10 to 30V per cell, the hardness is removed by more than 50% and the weakly- ionized species including the silica and the boron are removed by more than 90%.

[0053] The electrodeionization apparatus may have the same structure as the conventional electrodeionization apparatus except for the aforementioned constitutions.

[0054] The water to be fed into the electrodeionization apparatus of the present invention is preferable to be the water containing silica and/or boron prepared by treating the tap water, the river water, the ground water and the like with the reverse osmosis membrane apparatus.

[0055] The electrodeionization apparatus of the present invention is preferably operated in such a condition that the scale index SI is 500 or less. The scale index is obtained by the following expression: Scale Index SI = $[\text{Load per unit area of membrane of inorganic carbonate (mg-CO}_2/\text{hr}\cdot\text{dm}^2)] \cdot [\text{Ca}^{2+} \text{ concentration in concentrated water (mg-CaCO}_3/\text{L)}]$ wherein "Load of inorganic carbonate per unit area of membrane (mg-CO₂/hr·dm²)" is, as follows, a load (mg-CO₂/hr) per 1 dm² of the anion exchange membrane of the electrodeionization apparatus, and "Ca²⁺ concentration in concentrated water" is Ca²⁺ concentration (converted to CaCO₃) in the water flowing out of the concentrating compartment.

$$\text{Load per unit area of membrane of inorganic carbonate (mg-CO}_2/\text{hr}\cdot\text{dm}^2) = \frac{\left[\begin{array}{l} \text{concentration of CO}_2 \text{ in feed water (mg/L)} \\ \hline \text{area of anion exchange membrane (dm}^2\text{)} \end{array} \right]}{\left[\begin{array}{l} \text{flow rate of feed water in a compartment (L/hr)} \\ \hline \end{array} \right]}$$

[0056] The inventors of this invention conducted experiments for making clear the forming mechanism of scales in the electrodeionization apparatus. In the experiments, scales were intentionally formed by mixing excessive amounts of inorganic carbonate and Ca²⁺ in feed water to the electrodeionization apparatus. After that, the apparatus was disassembled and the concentrating compartment was observed. As a result, it was found that calcium carbonate adhered to the anion-exchange membrane at the concentrating compartment side.

[0057] Accordingly, the inventors presumed that the forming mechanism of scales was follows. That is, when the electrodeionization apparatus is in operation, pH near a surface of the anion-exchange membrane locally become alkaline. CO_3^{2-} or HCO_3^- and OH^- permeating the anion-exchange membrane from the diluting compartment are concentrated near the anion-exchange membrane. In addition, Ca^{2+} in water in the concentrating compartment is drawn or driven to the anion-exchange membrane, so that CO_3^{2-} or HCO_3^- and OH^- react with Ca^{2+} to form scales of calcium carbonate on the anion-exchange membrane.

[0058] The inventors further studied and found that no scale forms when the scale index SI obtained by multiplying the load per unit area of inorganic carbonate of the anion-exchange membrane by the Ca^{2+} concentration in concentrated water is 500 or less. The load of inorganic carbonate (mg- CO_2/hr) of the electrodeionization apparatus is obtained by multiplying the inorganic carbonate concentration (mg- CO_2/L) of water fed to the electrodeionization apparatus by the flow rate (L/hr). Therefore, the load of inorganic carbonate per unit area (mg- $\text{CO}_2/\text{hr-dm}^2$) is the product of [the inorganic carbonate concentration (mg- CO_2/L) of feed water] and [the flow rate per cell(L/hr) / the effective area of cells of the anion exchange membrane (dm^2)].

[0059] By controlling the scale index SI to be 500 or less, preferably 200 or less, precipitation of scales of calcium carbonate can be securely prevented in the concentrating compartment of the electrodeionization apparatus, thus enabling the stable operation of the electrodeionization apparatus for a long period of time.

[0060] In the electrodeionization apparatus, electric current more than the theoretical amount required to discharge ions from feed water is supplied to occur dissociation of water in the diluting compartments so as to continuously regenerate the ion exchanger. Therefore, increase in electric current to be supplied increases the alkalinity of the pH at the surfaces of anion-exchange membranes, facilitating the precipitation of calcium carbonate. Accordingly, the permissible SI varies according to the value of electric current.

[0061] In the electrodeionization apparatus which is directed to produce water having resistivity of about 10 M Ω -cm, the SI not exceeding 200, preferably not exceeding 150, is enough, when the required removing rate of silica is less 90% or when the current efficiency during its operation exceeds 20%. In view of economic consideration, the SI is preferably in a range between 80 and 200 to avoid treatment by a degassing apparatus, a softener, and/or such other extra device.

[0062] In case of electrodeionization apparatus in which the required removing rate of silica is 90% or more i.e. the current efficiency during its operation is 20% or less, the SI is preferably is 120 or less, particularly 80 or less. In view of economic consideration, the SI is preferably in a range between 50 and 120.

[0063] In case of electrodeionization apparatus in which the concentrating compartments are filled with the ion exchanger, the OH^- ions permeated the anion-exchange membrane are easy to move in the concentrating compartment, so that the scale is dispersed. In this case, the permissible SI is 80 or more even preferably 80-200 when the electric current is increased. The more preferable SI in this case is in a range between 80 and 150. If economic consideration is not taken, SI lower than 80 is also permissible.

[0064] To lower the SI to the specific value, there are some methods as follows. One of the methods is to lower the Ca^{2+} concentration in the concentrated water by removing Ca^{2+} by lowering the recovery of water or by the use of a Ca^{2+} removing device such as a softener. Another method is to lower the load on the membrane surface of the inorganic carbonate by reducing the amount of the water to be treated in the electrodeionization apparatus or removing inorganic carbonate by the use of a degassing device disposed at upstream of the electrodeionization apparatus. Alternative method of lowering the load on membrane surface of inorganic carbonate is to control the electric current of the electrodeionization apparatus.

[0065] As the electrodeionization apparatus of the present invention is operated with recovery of water 80% or more, the conductivity of water in the concentrating compartment should be high, thereby achieving excellent quality of treated water.

[0066] Water to be treated having CO_2 concentration of 10 ppm or less may be passed through a reverse osmosis apparatus before being introduced into the electrodeionization apparatus of the present invention.

[0067] In the present invention, the conductivity of the water in the concentrating compartments is preferable to be equal to or more than 50 $\mu\text{S}/\text{cm}$. The interrelationship between the conductivity and the electrical resistance of the concentrated water in the electrodeionization apparatus is shown in Fig.14. Fig.14 shows that the electrical resistance increases rapidly as the conductivity falls below 50 $\mu\text{S}/\text{cm}$. Therefore, the conductivity of at least 50 $\mu\text{S}/\text{cm}$ is required at the outlet of the concentrating compartments to ensure the electrical current. When the conductivity is below 50 $\mu\text{S}/\text{cm}$, the electrical resistance would increase to raise the electric cost.

[0068] Hereinafter, the apparatus for producing purified water of the present invention will be described in detail with reference to Fig.1 and Fig.2. Fig.1 and Fig.2 are invention respectively according to and embodiment.

[0069] The apparatus for producing purified water shown in Fig.1 is provided with a RO apparatus 2, a first preceding electrodeionization apparatus 3A and a second succeeding electrodeionization apparatus 3B which are connected in series. The apparatus for producing purified water shown in Fig.2 is provided with an activated carbon apparatus 1, RO apparatus 2, the preceding electrodeionization apparatus 3A, and the succeeding electrodeionization apparatus

3B which are connected in series.

[0070] The preceding electrodeionization apparatus 3A is related to the present invention mentioned above.

[0071] The succeeding electrodeionization apparatus 3B is conventional electrodeionization apparatus. The thickness of the diluting compartments of the succeeding electrodeionization apparatus 3B is preferable to be smaller than that of the preceding electrodeionization apparatus 3A and to be in the range of 2.0 to 6.0mm.

[0072] Any one of the succeeding electrodeionization apparatus may be that of the present invention, so that the purified water producing apparatus becomes to have a high flow rate and the purified water producing apparatus becomes compact in its constitution.

[0073] The electrodeionization apparatus of the present invention may have diluting compartments, each of which is divided into a plurality of cells by a partition member, and an ion exchanger is filled in the respective cells. At least a part of the partition member facing the cell is inclined relative to a normal flow direction of the water in the diluting compartment. The inclined part of the partition member allows permeation of the water, but prevents the ion exchanger to pass therethrough. Therefore, at least a part of the water flowing into the diluting compartment should flow obliquely relative to the normal flow direction of water, so that the water is dispersed overall the diluting compartment, thereby improving the contact efficiency between water and ion exchanger and improving the deionization property.

[0074] The water flows in the cells with being stirred by the inclined part of the member, so that a boundary layer of concentration along the surface of the membrane whereby a dispersion resistance of ions is lowered and the apparatus becomes possible to be operated with a high flow velocity.

[0075] In an aspect of the invention, the apparatus has a large number of cells are arranged vertically and laterally. A plurality of cells are arranged along the membrane surface both in the normal flow direction of water and a direction perpendicular to the normal flow direction, thereby extremely improving the contact efficiency between water and ion exchanger. Since the height of each cell is low, the ion exchanger is scarcely compressed. A vacancy is not formed at an upper portion in the cell, and the cell is filled evenly with the ion exchanger.

[0076] The configuration of each cell seen by projecting it upon the surface of the membrane is preferably a hexagon or a quadrangle. In case of the hexagon, the cells are preferably arranged in such a manner that a pair of sides thereof extend in the normal flow direction of water. In case of quadrangle, the cells are preferably arranged in such a manner that the respective sides thereof extend obliquely relative to the normal flow direction of water.

[0077] All of the cells may be filled with the same ion exchanger, or instead theréof some of the cells may be filled with ion exchanger different from the ion exchanger filled in the other cells. For example, an anion exchanger may be filled in first cells, a cation exchanger may be filled in second cells, and an amphoteric ion exchanger (or a mixture of the anion exchanger and the cation exchanger) may be filled in third cells.

[0078] This electrodeionization apparatus may be installed at the succeeding stage of the purified water producing apparatus of the present invention, whereby monovalent cations such as Na^+ leaked from the preceding stage are removed by the succeeding electrodeionization apparatus even when the feed water is fed at a high rate.

[0079] Hereinafter, other embodiments of the present invention will be described with reference to the attached drawings. Fig. 9 is an exploded perspective view showing the structure of a diluting compartment according to another embodiment, and Fig. 10 is a front view illustrating the water flowing condition of the partition member.

[0080] The diluting compartment comprises a rectangular frame 120, a partition member 121, preferably having conductivity, disposed in the frame 120, an ion exchanger 123 filled in cells 122 formed by the partition member 121, an anion-exchange membrane 124 and a cation exchange membrane 125 which are disposed to sandwich the frame 120. The partition member 121 may be electrically-conductive.

[0081] The frame 120 is provided with a flow inlet 126 for introducing raw water to be treated and a flow inlet 127 for concentrated water in an upper portion thereof and with a flow outlet 128 for deionized water and a flow outlet 129 for concentrated water formed in a lower portion thereof. The flow inlet 126 and the flow outlet 128 are connected to the inside of the frame 120 through a notch-like channels 126a, 128a, respectively.

[0082] Though only one channel 126a is illustrated to communicate with only the left top cell in Fig. 9, actually a plurality of channels 126a are formed in the upper portion of the frame 120 to uniformly distribute the raw water into the respective top cells aligned in the lateral direction, that is, the channels 126a directly communicate with the respective top cells. In the same manner, though only one channel 128a is illustrated to communicate with only the right bottom cell in Fig. 9, actually a plurality of channels 128a are formed in the lower portion of the frame 120 so as to directly communicate with the respective bottom cells.

[0083] The partition member 121 according to this embodiment is in a honeycomb form of a hexagonal shape in which a large number of cells are arranged in vertical and lateral directions in such a manner that a pair of sides of each cell 122 extend in the longitudinal direction of the frame 120, i.e. in the vertical direction. The vertical surfaces 131 may be permeable or not permeable to water.

[0084] When the vertical surfaces 131 are not permeable to water, uniform contact between water and the ion exchanger in the cells can be achieved so that the quality of product water is improved.

[0085] The other structure of the electrodeionization apparatus having this diluting compartment is the same as that

of the aforementioned conventional one of Fig. 12 and the flow passages for raw water, concentrated water, and electrode water are also the same as those of the conventional one.

[0086] As shown in Fig. 12, a cathode compartment is formed and defined by the cathode, the cathode spacer, and the cation-exchange membrane.

[0087] When the deionizing operation is conducted by passing raw water through this electrodeionization apparatus, the raw water introduced into the diluting compartment permeate the partition member 121 surrounding the cells 122 so as to flow into adjacent cells 122 and thus gradually flows downwardly. During this, the water is deionized. Finally, the water reaches the bottom of the diluting compartment and flows out to the flow outlet 128 through the channels 128a. Through the flow outlet 128, the water is took out from the electrodeionization apparatus as the deionized water.

[0088] The general direction of water in the diluting compartment is a downward vertical direction because the channels 126a for introducing raw water exist at the top of the frame 120 and the channels 128a for taking out the deionized water exist at the bottom of the frame 120. The partition 121 is inclined relative to the general direction of water exist at upper portions and lower portions of the respective cells, so that the water flows obliquely and downwardly from one cell 122 into the lower left cell 122 and the lower right cell 122. Therefore, the water flows substantially uniformly to all cells 122, thereby improving the contact efficiency between the water and the ion exchanger.

[0089] In this diluting compartment, since the cells 122 are relatively small, the downward pressure applied to the ion exchanger in each cell by the self weight of the ion exchanger and water pressure is low. Therefore, the ion exchanger is not compressed in any of the cells 122, thereby preventing the ion exchanger from being partially compressed at the lower portion of the cells.

20 [0090] Employed as the ion exchanger to be filled in the cells 122 may be an anion exchanger, a cation exchanger, an amphoteric ion exchanger, or a mixture of at least two of them.

[0091] Though the cells are hexagonal in Figs. 9 and 10, the cells may be quadrangular e.g. rhombic just like cells 145 shown in Fig. 11.

[0092] In the electrodeionization apparatus of the present invention, the projected area to the ion exchange membrane of the cells is preferably 1-100 cm², particularly 2-50 cm², more particularly 3-10 cm². As the size of the cells is reduced, the amount of the ion exchanger to be filled in one cell is reduced so that the fluidization of the ion exchanger is restrained. In addition, the strength of the partition member and the strength of the diluting compartment are increased. However, the pressure loss of the water flowing in the diluting compartment is increased.

[0093] The ion exchanger to be filled is normally an ion exchange resin. But the ion exchanger may be an ion exchange fiber, ion exchange non-woven fabric, or a mixture of an ion exchange resin and an ion exchange fiber. Ion conductor such as conductive resin may be employed.

[0094] When the thickness of the diluting compartments of preceding electrodeionization apparatus 3A is equal to or more than 7mm, particularly in the range of 8 to 30mm, and the thickness of the diluting compartments of the succeeding electrodeionization apparatus 3B is in the range of 2.0 to 6.0mm, the preceding electrodeionization apparatus 3A removes the weakly - ionized species including silica, boron, and the hardness, and the succeeding electrodeionization apparatus 3B further removes silica and boron. The succeeding electrodeionization apparatus 3B removes the alkalis leaked from the preceding electrodeionization apparatus 3A, the product water becomes high quality.

[0095] The water to be fed into the preceding electrodeionization apparatus is preferable to contain Na^+ of equal to or more than 0.1ppm as Na^+ . When the water is poor in Na^+ , the water is preferably added with NaCl .

[0096] To raise pH of the product water flown out of the preceding electrodeionization apparatus 3A, the feed water needs to contain Na^+ ion. The relationship between the concentration of Na^+ in the feed water and pH of the product water is shown in Fig.15. As shown in Fig.15, the concentration of Na^+ is required to be equal to or more than 0.1 ppm as Na^+ , preferably in the range of 0.5 to 4 ppm as Na^+ .

[0097] The concentration of CO_2 in the water to be fed into the preceding electrodeionization apparatus is preferable to be equal to or less than 3ppm as CO_2 .

[0098]. When the raw water contains a large amount of CO_2 which dissociates under alkaline condition, the removing rates of silica and boron decrease. When the concentration of CO_2 exceeds 3ppm, it is preferable to remove CO_2 by the use of a degassing apparatus installed in the upstream or by increasing pH of the water fed into the RO apparatus to 8 or more to form HCO_3^- :

[0099] The water recovery rate of preceding electrodeionization apparatus 3A is preferable to be 60 to 90%. Even when the water recovery rate of succeeding electrodeionization apparatus 3B is equal to or more than 95%, for example the rate is in the range of 95 to 99%, the product water of good quality is produced without causing scale.

[0100] As the electrical voltage and current applied to the preceding electrodeionization apparatus 3A are increased, pH of the water treated in the preceding electrodeionization apparatus becomes high. Therefore, it is preferable to observe pH by installing a pH meter 4 to the pipe for discharging the treated water from preceding electrodeionization apparatus 3A and to control the voltage and the current applied to the preceding electrodeionization apparatus 3A so that the value of pH becomes preferably equal to or more than 8.5, more preferably between 9.0 and 10.5. The preceding electrodeionization apparatus 3A is preferable to remove Na^+ at a rate of less than 90% and the chloride ion of more

than 95%. When the chloride removing rate is more than 95%, pH becomes high.

[0101] It is preferable that a resistivity meter 5 and a silica meter 6 are installed to the pipe for discharging the product water from the succeeding electrodeionization apparatus 3B in order to observe the resistivity and the concentration of silica of the water product in the succeeding electrodeionization apparatus 3B, and the voltage and the current applied to the apparatus 3A and /or the apparatus 3B are controlled so that the resistivity and the concentration of the silica are in the sights.

[0102] When the electrodeionization apparatuses 3A, 3B are operated at $A/(Q \cdot SV)$ of equal to or more than 4000, the removing rates of the silica and the boron are increased.

[0103] The "A", "Q", and "SV" are as follows:

10 A: the operational current (A);

Q: the flow rate of the feed water per cell in the diluting compartments (L/sec), where "L" is liter; and

SV: the flow rate of the feed water per ion exchangers in the diluting compartments (L/L - ion exchangers.sec).

15 [0104] The removal rate of silica is closely related to the value of $A/(Q \cdot SV)$. $A/(Q \cdot SV)$ of 4000 or more can achieve the silica removing rate of 97% or more.

[0105] The apparatus for producing purified water of the present invention may be provided with a RO apparatus, a degassing apparatus where the permeating water passing through the RO apparatus is introduced, and the electrodeionization apparatus where the water treated in the degassing apparatus is introduced. It is preferable that the feed water having M - alkalinity expressed as $CaCO_3$ of more than 20 ppm and pH of or more than 6.5 is fed to the RO apparatus, and that the water having pH of less than 6.2 is taken out from the RO apparatus and fed into the degassing apparatus.

[0106] It is preferable that the degassing apparatus is a membrane degassing apparatus and the water to be introduced to the degassing apparatus has TOC of less than 200ppb or conductivity of less than 20 $\mu S/cm$.

20 [0107] The M - alkalinity of the feed water is removed by the RO apparatus, so that the permeating water thereof has low pH. The water having low pH is efficiently removed in CO_2 by the degassing apparatus, so that the electrodeionization apparatus can be reduced in the load of CO_2 loaded thereon.

[0108] The ability to remove CO_2 can be improved by 30 to 50% by degassing the water which is decreased in pH by treating with the RO apparatus in comparison with the case where the water is degassed before the treatment with the RO apparatus.

25 [0109] Particularly when the membrane degassing apparatus is employed for the degassing apparatus, the degassing apparatus arranged behind the RO apparatus can stabilize the ability to degas for a long period of time.

[0110] This is because the RO apparatus removes salts and TOC (total organic carbon), so that a slime defects caused by the salts and the TOC are avoided. It is preferable that the feed water into the membrane degassing apparatus has the TOC concentration of less than 200ppb, and/or the electric conductivity of 20 $\mu S/cm$ in order to prevent the membrane from contamination and to stabilize the degassing ability for a long period.

30 [0111] The reject water of the RO apparatus 2 is discharged as the drain and the permeated water of the RO apparatus 2 is distributed and fed into the electrode compartment 3Aa, the diluting compartments 3Ab and concentrating compartments 3Ac of the preceding electrodeionization apparatus 3A respectively. The product water of the preceding electrodeionization apparatus 3A (the water flowing out from the diluting compartments 3Ab) is distributed and fed into the electrode compartment 3Ba, the diluting compartments 3Bb and the concentrating compartments 3Bc of the succeeding electrodeionization apparatus 3B respectively. The water flowing out from the diluting compartments 3Bb is discharged as the product water. The water flowing out from the electrode compartments 3Aa and 3Ba is discharged as the drain.

35 [0112] The concentrated water flowing out from the concentrating compartments 3Ac of the preceding electrodeionization apparatus 3A is acidic, and the concentrated water flowing out from the concentrating compartments 3Bc of the succeeding electrodeionization apparatus 3B is alkaline. Therefore, it is preferable that the concentrated water flowing out from the concentrating compartments 3Ac and 3Bc are mixed and returned to the inlet portion of the RO apparatus 2.

40 [0113] The concentrated water of either preceding electrodeionization apparatus 3A or succeeding electrodeionization apparatus 3B may be independently fed back to the front stage of the RO apparatus 2. The concentrated water of the succeeding electrodeionization apparatus 3B may be fed back to the inlet portion of the preceding electrodeionization apparatus 3A.

45 [0114] While the electrodeionization apparatus shown in Fig.1 and Fig.2 has one electrodeionization apparatus 3B, the electrodeionization apparatus may be provided with two or more electrodeionization apparatuses 3B which are connected in series.

50 [0115] As shown in Fig.7 and Fig.8, cells 23 of more than 7mm in the thickness of diluting compartments and cells 24 of less than 7mm in the thickness of the diluting compartments may be arranged between anode 21 (or 21A,

21B) and a cathode 22 so that the fed water flows through these cells in series.

5 [0116] The electrodeionization apparatus of the present invention is preferably operated so that the concentration of silica of the concentrated water flowing out from the concentrating compartments of the second or later electrodeionization apparatus is less than one thousand times as high as that of the produced water of the electrodeionization apparatus. In order to lower the concentration of silica of the produced water to 0.1 ppb or less, the concentration of silica of the concentrated water is preferable to be decreased to 100ppb or less.

10 [0117] When the electrodeionization apparatus is operated in this manner, since the concentration gradient of silica from the concentrating compartments to the diluting compartments is relatively low even in the vicinity of the outlet of the concentrating compartments, the diffusion of silica from the concentrating compartments to the diluting compartments is retarded so that the concentration of silica of the produced water is reduced.

15 [0118] In the present invention, the apparatus for producing purified water may be composed of a RO apparatus, a first electrodeionization apparatus and a second electrodeionization apparatus so that the water firstly flows from a reverse osmosis membrane apparatus into the first apparatus and then flows into the second electrodeionization apparatus wherein the reverse osmosis membrane apparatus consists of the reverse osmosis membrane having the degree of desalination of monovalent salts of equal to or less than 97%.

20 [0119] Hereinafter, "the degree of desalination of monovalent salts" will be simply called as "the degree of the desalination".

25 [0120] As shown in Fig.14 mentioned above, the electrical resistance rapidly increases as the conductivity of the concentrated water of the electrodeionization apparatus falls below 50 $\mu\text{S}/\text{cm}$. The conductivity of more than 50 $\mu\text{S}/\text{cm}$, preferably more than 75 $\mu\text{S}/\text{cm}$ reduces the electrical resistance and sufficiently ensures the electrical current required for deionization in the electrodeionization apparatus.

30 [0121] When usual tap water or industrial water having the conductivity of about 200 $\mu\text{S}/\text{cm}$ is fed into the RO apparatus installed with the RO membrane having the degree of desalination of 97%, and the water is treated under water recovery of 75 %, the conductivity of the water permeated through the RO membrane is defined as follows.

$$(Conductivity of the water permeating through RO membrane) = (200 + 800) / 2(1 - 0.97) = 15 \mu\text{S}/\text{cm}$$

35 [0122] When the electrodeionization apparatus is operated at the water recovery of 80 % by feeding the above water permeated through the RO membrane, the conductivity of the concentrated water is $15 \times 5 = 75 \mu\text{S}/\text{cm}$.

40 [0123] While the conductivity of the concentrated water varies depending on the conductivity of the raw water to be fed into the RO apparatus, the water recovery of the electrodeionization apparatus, by employing the RO membrane having the degree of desalination of equal to or less than 97%, the concentrated water can be provided with the conductivity of roughly 75 $\mu\text{S}/\text{cm}$ or more in operation employing the usual raw water and the usual water recovery and the electrical current can be ensured in the electrodeionization apparatus.

45 [0124] In the present invention, it is very important to feed the permeating water obtained by treating the feed water by RO membrane having relatively low degree of desalination into the diluting compartments since the conductivity of the concentrated water can not be ensured when the permeating water is fed into the concentrating compartments alone, and the results prevent decrease of the electrical resistance and improvement of the electrical current.

50 [0125] Furthermore, the RO membrane preferably has the removal rate of the hardness and silica of equal to or more than 97%. That is, the hardness such as by Ca^{2+} and silica easily form scales in the electrodeionization apparatus and require the appreciably electrical current to remove the scales. Therefore, the hardness and silica are preferably removed in the RO apparatus preceding the electrodeionization apparatus, so that the RO membrane having the removal rate of the hardness and silica of more than 97% is preferable to be employed.

55 [0126] The RO membrane mentioned above may be commercially sold one. It may be prepared by being treated with oxidizer so that the RO membrane becomes hydrophilic and has the degree of desalination of equal to or less than 97% and the removal rate of silica of equal to or more than 97%.

[0127] In the present invention, the electrodeionization apparatus is preferably provided with the diluting compartments having a thickness of equal to or more than 7mm.

60 [0128] That is, when the permeate water of the RO apparatus in which NaCl and the like remains is fed into the electrodeionization apparatus wherein the diluting compartments having a large thickness as above is employed and wherein the ion exchange layer comprising the anion exchanger alone or mixture of the anion exchanger and the cation exchanger is filled in the diluting compartments, the conductivity of the product water (deionized water) is almost same as of the fed water or slightly larger than it, while carbon dioxide gas (CO_2) and anions are removed and about 90% of silica and boron are also removed. Besides, the hardness including Ca^{2+} , Mg^{2+} is further removed. However, since the monovalent cations including Na^+ , K^+ are inferior in the removal rate so that the alkalis including NaOH and KOH which have large molar conductivity are to be leaked into the product water, and the product water tends to be increased in pH and slightly in conductivity.

[0129] For the same reason as above, since OH⁻ is difficult to be discharged and H⁺ is easy to be discharged in the concentrating cells, pH becomes acidic therein so that the scale is not formed even when Ca²⁺, Mg²⁺ and the like are concentrated at high concentration.

[0130] Specifically, in order to decrease the electrical resistant and to increase the electrical current of the electrodeionization apparatus, the electrodeionization apparatus is increased in the conductivity of the concentrated water by employing the RO membrane having the degree of desalination of monovalent salts represented by NaCl of equal to or less than 97 % to leak the monovalent salts into the RO permeating water so that the permeated water is fed into the diluting compartments of the electrodeionization apparatus. When the degree of desalination of RO membrane exceeds 97%, the aforementioned effect is not sufficiently achieved.

[0131] While the degree of desalination of the RO membrane is preferable to be low for the purpose of increasing the conductivity of the concentrated water of the electrodeionization apparatus so as to decrease the electrical resistance and to improve the electrical current of the electrodeionization apparatus, when the degree of desalination is unduly decreased, the decrease of the current is small and, rather, the load on the electrodeionization apparatus increases because of degradation of the quality of the feed water so that the product water (deionized water) is degraded in its quality. Therefore, RO membrane is preferably to have the degree of desalination especially of 90 to 95 %.

[0132] The RO membrane as the above may employ a membrane being marketed as low desalination membrane, for example a membrane called as a loose RO membrane and a nano - filtration (NF membrane) membrane, specifically, "LES 90" and "NTR-729HF" produced by Nitto Electrical Industry Co., Ltd.

[0133] In the present invention, the RO membrane is also preferably to have the removal rate of the hardness and silica, more preferably besides the removal of silica, more preferably besides the removal rate of TOC (total organic carbon) of equal to or more than 97 %.

[0134] In the preceding electrodeionization apparatus of the purified water producing apparatus of the present invention, by the same reason as above, the electrodeionization apparatus is preferable to be provided with the diluting compartments having a thickness of equal to or more than 7mm, particularly of 8 to 30mm.

[0135] The ion exchanger is most preferable to be a mixture of the anion exchanger and the cation exchanger. When the applied current is increased, a single layer comprising the anion exchanger alone can bring the same effect as the mixture. Of course, a combination of the mixture and the anion exchanger may be employed.

[0136] In the present invention, an ultraviolet - light irradiating apparatus may be installed between electrodeionization apparatuses to decompose TOC in the water.

[0137] When the product water of the preceding electrodeionization apparatus is alkaline, the ultraviolet - light irradiating apparatus decomposes TOC at high efficiency. When hydrogen peroxide or ozone having concentration of 2 to 20 times as high as the concentration of TOC in the water is added into the product water, the efficiency of decomposition is further increased.

[0138] In the present invention, a first RO apparatus may be installed before the preceding electrodeionization apparatus, and a second RO apparatus may be installed between the preceding electrodeionization apparatus and the succeeding electrodeionization apparatus.

[0139] By using the RO apparatus, silica and boron are easily removed from the alkaline feed water. Since the product water flowing out from the preceding electrodeionization apparatus is alkaline without adding alkalis including NaOH, the second RO apparatus easily removes silica and boron from the product water.

[0140] For example, in the apparatus comprising the first RO apparatus, the preceding electrodeionization apparatus, the second RO apparatus and the succeeding electrodeionization apparatus which are arranged in this order and connected in series, when the water flowing into the second RO apparatus has pH of 7, the second RO apparatus removes 99% of silica and 70% of boron in the water. When the water flowing into the second RO apparatus has pH of 9, the second RO apparatus removes 99.9% of silica and 97% of boron.

[0141] In the apparatus comprising the preceding electrodeionization apparatus and the succeeding electrodeionization apparatus which are connected in series, when water containing silica in a high concentration is fed into the apparatus momentarily, silica accumulates and the removal rate of silica may decrease even after the silica content of the feed water decreases down to usual. Therefore, the feed water fed into the preceding electrodeionization apparatus may be regularly added with salts including NaCl so that silica accumulated in the electrodeionization apparatus can be discharged therefrom.

[0142] By adding the salts as above, at least one of the following requirements (i), (ii), and (iii) is preferable to be achieved for 5 to 48 hours:

- (i) To set the conductivity of the feed water flowing into preceding electrodeionization apparatus for more than 15 μ S/cm;
- (ii) To set the concentration of Na⁺ ion of the water flowing into the preceding electrodeionization apparatus for more than 3ppm; and
- (iii) To set pH of the product water flowing out preceding electrodeionization apparatus for more than 9.8

[0143] Fig.15 shows an example of the interrelationship between pH values of the feed water fed into the preceding electrodeionization apparatus and the product water flowing out from the therefrom.

[0144] It is further effective heat the feed water fed into the electrodeionization apparatus to more than 35°C besides to add the salts including NaCl to the feed water.

[0145] In the conventional electrodeionization apparatus, slime is frequently formed whereby the differential pressure of the concentrating compartments rises to prevent the operation. In the two - stages electrodeionization apparatus of the present invention, the concentrated water of the preceding electrodeionization apparatus becomes acidic and the concentrated water of the succeeding electrodeionization apparatus becomes basic without adding agents so that the slime is not be formed in the concentrating compartments. Even after six months operation, when the feed water including 10,000 of living bacteria per milli liter is fed into the preceding electrodeionization apparatus, the concentrated water of the preceding electrodeionization apparatus is decreased in number of the living bacteria to 100 per milliliter and the concentrated water of the succeeding electrodeionization apparatus is decreased in number of the living bacteria to 0 per milliliter.

[0146] To raise the removal rate of silica, the alkaline chemicals may be added into the water between the first and second stages or the inlet of the first stage. Even when pH of the water is not sufficiently increased at the first stage, the treatment with the second or later electrodeionization apparatus improves the removal rate of silica.

[0147] The feed water fed into the first electrodeionization apparatus is preferable to have pH of equal to or more than 9.5 in order to efficiently remove the weakly - ionized species including silica and boron by the second or later electrodeionization apparatus. Although the removal rate of silica is 99% when the feed water fed into the secondary electrodeionization apparatus has pH of 9.0, the removal rate of silica is 99.9% when the feed water fed into the secondary electrodeionization apparatus has pH of 9.5.

[0148] In the second or later electrodeionization apparatus, the Ca^{2+} concentration in the feed water is preferable to be equal to or less than 30ppb, more preferable to be equal to or less than 5ppb as Ca^{2+} since the water flowing in the concentrating compartments and the electrode compartment is alkaline. In the second or later electrodeionization apparatus, the basic feed water causes the scale of CaCO_3 in the concentrating compartments and the electrode compartment. Therefore, Ca^{2+} is required to be removed at the first stage.

Examples and Comparative Examples

[0149] The following shows the apparatuses used in Examples and Comparative Examples. In Examples 1 to 5 and Comparative Examples 1 to 3, the apparatuses are arranged as shown in Fig.4 to be connected in series. In Example 6, the apparatus including two electrodeionization apparatuses are arranged as shown in Fig. 2 to be connected in series.

- 35 1) Activated carbon apparatus
: "Kuricoal KW 10-30" produced by Kurita Water Industries Ltd.
- 2) RO apparatus
: "Maku-Ace KN 200" produced by Kurita Water Industries Ltd.
- 3) Electrodeionization apparatus "Pure-Ace PA-200" produced by Kurita Water Industries Ltd.
40 flow rate of product : 100 liters per hour

Comparative Example 1

[0150] An electrodeionization apparatus is assembled as shown in Fig.3 in which the following ion exchange membranes are employed and the diluting compartments are filled with mixture of 6 parts by volume of the following anion exchange resin and 4 parts by volume of the following cation exchange resin.

[0151] The anion exchange resin and the cation exchange resin are sufficiently washed by ultra pure water before being filled in the diluting compartments. Each of the diluting compartments has a thickness of 2.5 mm and consists of 12 cells.

[0152] The water is fed into the electrodeionization apparatus under conditions as shown in Table 1. The resistivity of the product water, the concentration and the removal rate of silica, boron and the other ions are measured and results are shown in Table 1.

- [0153] Anion exchange membrane : "Neosepta AHA" produced by Tokuyama Co., Ltd
- [0154] Cation exchange membrane : "Neosepta CMB" produced by Tokuyama Co., Ltd.
- [0155] : Anion exchange membrane "SA 10A" produced by Mitsubishi Chemical Corporation.
- [0156] : Anion exchange membrane "SK 1B" produced by Mitsubishi Chemical Corporation.

Example 1

5 [0157] An electrodeionization apparatus is assembled to conduct the treatment in the same manner as comparative example 1 except that each of the diluting compartments has thickness of 10 mm and consists of three cells, and the water is fed under conditions as shown in Table 1. The resistivity of the product water, the concentrated and the removal rate of silica, boron and the other ions are shown Table 1.

[0158] Further, the variation in pH with the applied voltage is shown in Fig.5.

10 [0159] The CO_2 concentration of the feed water and the CO_2 concentration of the water treated by the preceding electrodeionization apparatus 3A are measured to calculate the removal rate. When the CO_2 concentration of the feed water is 1ppm, the removal rate is 90%, and when the CO_2 concentration of the feed water is 4ppm, the removal rate is 60% or less.

[0160] In Example 1, by employing the heterogeneous membrane for the ion exchange membrane, the removing rate of Na^+ decreases from 46% to 40% and pH increases from 9.5 to 9.65.

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Table 1.

| | | Comparative Example 1 | Example 1 |
|--------------------------|---|--------------------------|-----------|
| feeding condition | number of cells [-] | 12 | 3 |
| | thickness of diluting compartment [mm] | 2.5 | 10 |
| | electric voltage [V] | 54 | 45.9 |
| | electric current [A] | 0.8 | 2 |
| | water recovery [%] | 90 | 90 |
| | SV in concentrating compartment [hr ⁻¹] | 60 | 60 |
| | pH of feed water [-] | 7 | 7 |
| | conductivity of feed water [μ S/cm] | 10 | 10 |
| | silica concentration of feed water [ppb as SiO ₂] | 200 | 200 |
| | boron concentration of feed water [ppb as B] | 19 | 20 |
| | sodium concentration of feed water [ppb as Na] | 1.6 | 1.6 |
| | chloride ion concentration of feed water [ppb as Cl] | 2 | 2 |
| quality of product water | calcium concentration of feed water [ppb as Ca] | 50 | 50 |
| | pH of product water [-] | 7 (pure water) | 9.5 |
| | resistivity of product water [M Ω · cm] | 16.5 | 0.1 |
| | silica concentration of product water [ppb as SiO ₂] | 52 | 18 |
| | removal rate of silica [%] | 74 | 91 |
| | boron concentration of product water [ppb as B] | 5.2 | 2.5 |
| | removal rate of boron [%] | 72.6 | 87.5 |
| | sodium concentration of product water [ppb as Na] | 0.2 | 860 |
| | chloride ion concentration of product water [ppb as Cl] | <0.1 | 10 |
| | calcium concentration of product water [ppb as Ca] | <1.0 | <1.0 |

Examples 2 to 5, Comparative Examples 2, 3

[0161] Electrodeionization apparatuses are assembled in the same manner as Comparative Example 1 except that

the diluting compartments of those respectively have thickness as follows. The water is treated under the same conditions as Comparative Example 1 except that the water is fed at SV of 60 per hour, and the electric voltage as the current efficiency falls in the range of 10 to 20%. The resistivity and pH of the product water are shown in Fig.6.

5 Comparative Example 2 : 2.5mm
 Comparative Example 3 : 5.0 mm
 Example 2 : 7.0 mm
 Example 3 : 10.0 mm
 Example 4 : 15 mm
 10 Example 5 : 30 mm

Example 6

15 [0162] As shown in Fig.2, the activated carbon apparatus 1, the RO apparatus 2 and the electrodeionization apparatus 3A, 3B are arranged in this order to be connected in series wherein the preceding electrodeionization apparatus 3A is the same electrodeionization apparatus provided with the diluting compartments having a thickness of 10mm as Example 1 and the succeeding electrodeionization apparatus 3B is the same electrodeionization apparatus provided with the diluting compartments having thickness of 2.5mm as Comparative Example 1. Then, the feed water is fed into the apparatus under conditions as shown in Table2. The quality of the product water (flowing out from the electrodeionization apparatuses 3A, 3B respectively) are shown in Table2.

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Table 2.

| | | preceding electrodeionization apparatus 3A | succeeding electrodeionization apparatus 3B |
|----|--|--|---|
| 30 | number of cells [-] | 3 | 12 |
| | thickness of diluting compartment [mm] | 10 | 2.5 |
| | electric voltage [V] | 45.9 | 54 |
| | electric current [A] | 2 | 1 |
| | water recovery [%] | 90 | 95 |
| 35 | pH of product water [-] | 9.5 | 7 |
| | resistivity of product water [$M\Omega \cdot cm$] | 0.1 | 18.2 |
| | silica concentration of product water [ppb as SiO_2] | 18 | <0.1 |
| | boron concentration of product water [ppb as B] | 2.5 | <0.05 |

[0163] The results show the followings:

55 [0164] As shown in Table 1, the electrodeionization apparatus of Example 1 provided with the diluting compartments having a thickness of 10mm slightly exceeds the electrodeionization apparatus of Comparative Example 1 provided with the diluting compartments having a thickness of 2.5mm in the removal rate of silica and boron. Calcium is almost entirely removed. As shown in Fig. 5, in the electrodeionization apparatus provided with the diluting compartments having a thickness of 10mm, pH of the product water increases as the applied voltage increases.

[0165] As shown in Fig.6, as the thickness of the diluting compartments exceeds 7mm, the resistivity of the product water deteriorates to raise pH of the product water.

5 [0166] In the preceding electrodeionization apparatus 3A, the cells are applied with the voltage at 8V per cell, and in the succeeding electrodeionization apparatus 3B the cells are applied with the voltage at 3V per cell. When the conventional electrodeionization apparatuses are employed, the cells of the preceding electrodeionization apparatus are applied with the voltage of 15V and those of the succeeding electrodeionization apparatus are applied with the voltage of 4.5V.

10 [0167] Table 2 shows that when the water is firstly treated in the electrodeionization apparatus provided with the diluting compartments having a thickness of 10mm and then fed into the electrodeionization apparatus provided with the diluting compartments having a thickness of 2.5mm, the concentration of silica and boron is lowered to the limit of analytic detection, and the product water of very good quality (pH 7 and the resistivity of 18.2 MΩ · cm) can be contained.

Example 7

15 [0168] The purified water producing apparatus shown in Fig.13 is assembled. The succeeding electrodeionization apparatus relates to the present invention which is provided with the cells having honeycomb structure in the diluting compartments. The product water flown out of the preceding electrodeionization apparatus is of the following quality:

pH : 9.5

20 conductivity : 13 µS/cm

concentration of silica : 18 ppb

concentration of boron : 2.5 ppb

25 [0169] For comparison, the succeeding electrodeionization apparatus is substituted for the conventional electrodeionization apparatus provided with ribs in the diluting compartments.

[0170] Operational conditions and results are shown in Table 3.

[0171] The measuring conditions are as follows

[measuring condition]

30 [0172] The cells of the electrodeionization apparatus : Hexagonal form, the area of which is 3.9 cm².

[0173] Spacing between ribs : 28mm

35 [0174] Ion exchange resin of the diluting compartments : SA 10A of anion resin and SK 1B of cation resin; both of which are produced by Mitsubishi Chemical Corporation; (including 6 parts of the anion exchange resin and 4 parts of the cation exchange resin)

[0175] Ion exchange membrane : AHA (anion exchange membrane), CMB (cation exchange membrane) produced by Tokuyama Co., Ltd.

[0176] The operating conditions are shown in Table 3.

Table 3.

| | Example 7 | (For comparison) |
|--|-----------|------------------|
| number of cells | 4 | 12 |
| thickness of diluting compartment (mm) | 5.0 | 2.5 |
| height of cell (cm) | 400 | 600 |
| Space velocity (hr ⁻¹) | 120 | 60 |
| voltage applied (V) | 25 | 54 |
| current flown (A) | 2.5 | 1.0 |
| resistivity of product water (MΩ · cm) | 18.2 | 18.2 |
| SiO ₂ concentration in product water flown out of succeeding electrodeionization apparatus (ppb as SiO ₂) | <0.1 | <0.1 |
| B concentration in product water flown out of succeeding electrodeionization apparatus (ppb as B) | < 0.05 | < 0.05 |

[0177] As clearly shown by Table.3, the apparatus of the present invention provides the product water of high quality at a higher rate than the comparison one. It is also shown that apparatus of the present invention has the small height and is very compact.

5 Example 8, Comparative Example 4

[0178] In Example 8 and Comparative Example 4, the apparatus for producing purified water in which the following activated carbon apparatus, RO membrane apparatus, and two electrodeionization apparatus are connected in series are used.

10 [0179] Activated carbon apparatus : "Kuricoal KW10-30" produced by Kurita Water Industries Ltd.

[0180] RO membrane apparatus : "Maku-Ace KN200" produced by Kurita Water Industries Ltd.

[0181] Electrodeionization apparatus : "Pure-Ace PA-200" produced by Kurita Water Industries Ltd.

flow rate of product : 100 liters per hour

15 [0182] The electrodeionization apparatuses are assembled as shown Fig.1 wherein the following ion exchange membranes are employed in the aforementioned electrodeionization apparatus, the diluting compartments are filled with the mixture of the ion exchange resins composed of 6 parts by volume of the following anion exchange resin and 4 parts by volume of the following cation exchange resin. The anion exchange resin and cation exchange resin are sufficiently washed by the ultra - pure water before they are filled into the diluting compartments.

20 [0183] Two types of electrodeionization apparatuses one of which is an electrodeionization apparatus "B" provided with the diluting compartments having a thickness W of 2.5 mm and consisting of 12 cells, and the other of which is an electrodeionization apparatus "A" provided with the diluting compartments having a thickness W of 10 mm and consisting of 3 cells are assembled.

[0184] Anion exchange membrane : "Neosepta AHA" produced by Tokuyama Co., Ltd.

[0185] Cation exchange membrane : "Neosepta CMB" produced by Tokuyama Co., Ltd.

25 [0186] Anion exchange resin : "SA 10A" produced by Mitsubishi Chemical Corporation.

[0187] Cation electrodeionization apparatus : "SK 1B" produced by Mitsubishi Chemical Corporation.

30 [0188] The RO apparatus employs the RO membrane shown in Table 4 and the electrodeionization apparatus composed of the electrodeionization apparatus "A" and electrodeionization apparatus "B" which are connected together in series. The treatment is conducted under conditions where the flow rate of product is 100 liters per hour, the water flows in the electrodeionization apparatus at SV of 70 per hour, the recovery of the water in the RO apparatus is 75%, and the recovery of water in the electrodeionization apparatus 80%. The measurement of the water quality in the RO apparatus , and the voltage, the current and the water quality in the electrodeionization apparatus are shown in Table 4.

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Table 4.

| | | Example 8 | Comparative Example 4 |
|------------------------------------|--|-----------------------------------|---|
| RO membrane apparatus | type of RO membrane | | Hydrophilic "SUL-G10" produced by Toray Co., Ltd. * |
| | performance of RO membrane | Na ⁺ removal rate [%] | 93.0 |
| | | Cl ⁻ removal rate [%] | 97.5 |
| | | Ca ²⁺ removal rate [%] | 99.6 |
| | | silica removal rate [%] | 99.5 |
| | pH of feed water | | 6.5 |
| | conductivity of feed water [μ S/cm] | | 160 |
| | conductivity of permeating water [μ S/cm] | | 25 |
| | electric current [A] | | 1.5 |
| | electric voltage [V] | | 30 |
| electrodeionization apparatus A | conductivity of product water [μ S/cm] | | 30 |
| | pH | | 9.8 |
| | silica removal rate [%] | | >98 |
| | electric current [A] | | 1.0 |
| | electric voltage [V] | | 30 |
| electrodeionization apparatus B | silica removal rate [%] | | >98 |
| | resistivity of product water [$M\Omega \cdot cm$] | | 18.2 |
| | | | 15 |

* : This membrane is prepared in such a manner that the "SUL-G10" membrane is immersed in a solution consisting of purified water and sodium hypochlorite of 1000ppm (expressed as Cl₂), and the solution is circuralted for 24 hours so as to be hydrophilic.

[0189] According to Table 4, in Comparative Example 4 wherein the RO membrane having high degree of diluting is employed, the current hardly flows and the quality of the product water is scarcely improved in the electrodeionization

apparatus. In contrast, in Example 8, the apparatus employing the RO membrane having the degree of diluting of equal to or less than 97%, preferably further having the removal rate of the hardness and the silica of equal to or more than 97%, and employing the diluting compartments having a thickness of equal to or more than 7mm to achieves high quality of the product water by large current and diluting efficiency.

5 Example 9

[0190] The electrodeionization apparatus of Example 1 shown in Table 1, and ultraviolet-light irradiating apparatus provided with two UV lamps ("AZ-26 (0.1 kW)" produced by Japan Photo Science Co., Ltd.), and the succeeding electrodeionization apparatus 3B shown in Table 2 are arranged in this order and connected in series. Raw water having TOC of 300ppb is fed into the apparatuses. The product water flowing out of the preceding electrodeionization apparatus has pH of 9.5.

[0191] The measurements of TOC concentration of the product water flowing out of each electrodeionization apparatus are shown in Table 5.

15 Table 5.

| | Example 9 | Example 10 | Comparative Example 5 |
|--|-----------|------------|-----------------------|
| 20 TOC of product water of preceding electrodeionization apparatus [ppb] | 55 | 55 | 70 |
| TOC of product water of succeeding electrodeionization apparatus [ppb] | 2.5 | 1.1 | 10 |
| TOC of raw water : 300ppb | | | |

25 Example 10

[0192] In Example 9, H_2O_2 is added to the product water flowing out from the preceding electrodeionization apparatus to set the concentration in the water for 1ppm. The measurements of TOC are shown in Table 5.

30 Comparative Example 5

[0193] Treatment is made in the same manner as Example 9 except that the electrodeionization apparatus of Comparative Example 1 shown in Table 1 is employed for preceding electrodeionization apparatus and NaCl added to the product water flowing out from the preceding electrodeionization apparatus to measure the TOC. The measurements of TOC are also shown in Table 4.

[0194] In this treatment, NaCl is added in order to increase the conductivity to about 15 $\mu S/cm$. In Examples 9 and 10, the conductivity of the feed water flowing out from the preceding electrodeionization apparatus is about 15 $\mu S/cm$.

[0195] As shown Table 5, according to the present invention, the concentration of TOC is sufficiently lowered.

40 Example 11

[0196] The apparatus of Example 6 is inspected about influence of foul by silica, and a method of recovery thereof is searched.

45 Step 1

[0197] When raw water having concentration of silica of 10,000ppb is continuously fed into the apparatus of Example 6 for 24 hours, the concentration of silica of the product water flowing out from the preceding electrodeionization apparatus becomes 150ppb, and that of the product water flowing out from the succeeding electrodeionization apparatus becomes 15ppb.

50 Step 2

[0198] Then, feed water is changed to contain silica at a concentration of 200ppb, and NaCl is added to the feed water to be fed into the preceding electrodeionization apparatus for 24 hours so as to set the conductivity of the feed water for 25 to 30 μS , pH of the water flowing out from the preceding electrodeionization apparatus for 10 to 10.2, the electrical voltage applied to the preceding electrodeionization apparatus for 35.2V, the current applied to the preceding

electrodeionization apparatus for 2A, the electrical voltage applied to the succeeding electrodeionization apparatus for 41V, and the current applied to the succeeding electrodeionization apparatus for 1A. 3days after, the concentration of silica of the product water flowing out from the preceding electrodeionization apparatus becomes 25ppb, and that of the product water flowing out from the succeeding electrodeionization apparatus becomes 0.2ppb.

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Comparative Example 6

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[0199] The same experiment as Example 11 is conducted except that in the above step 2, NaCl is not added. As the result thereof, the silica concentration of the product water flowing out from the succeeding electrodeionization apparatus becomes 2.5 ppb which is extremely higher than in Example 6.

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[0200] Table 6 shows the results of Example 11 and Comparative Example 6.

Table 6.

| | at a normal state | under fouled condition (24hours) | normal state(3days after) | | |
|--|-------------------|----------------------------------|---------------------------|------------|------------|
| | | | Comparative Example 6 | Example 11 | Example 12 |
| Concentration of silica in feed water | 200 | 10,000 | 200 | 200 | 200 |
| Concentration of silica in product water flown out of the preceding electrodeionization apparatus [ppb] | 18 | 150 | 50 | 25 | 15 |
| Concentration of silica in product water flown out of the succeeding electrodeionization apparatus [ppb] | <0.1 | 15 | 2.5 | 0.2 | <0.1 |

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Example 12

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[0201] In Example 11, the feed water fed into the preceding electrodeionization apparatus is heated to 40°C besides addition of salt to the feed water. As the result, the silica concentration of the product water flowing out from the preceding electrodeionization apparatus is lowered to 15ppb and that of the product water flowing out from the succeeding electrodeionization apparatus is lowered to less than 0.1ppb.

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Industrial capability of the invention

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[0202] As described above, according to the diluting compartments of the present invention, the weakly - ionized species having high dissociation constant such as silica and boron are efficiently removed without need of adding alkaline agent and without formation scale.

[0203] According to the apparatus for producing purified water of the present invention, by employing the multi - staged electrodeionization apparatuses the first of which relates to the present invention, the pure water of high purity is easily and efficiently produced, and the apparatus for producing purified water is provided at low cost.

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Claims

1. An electrodeionization apparatus comprising:

a cathode;
an anode;

concentrating compartments and diluting compartments alternately formed by arranging a plurality of cation exchangers and anion exchangers between the cathode and the anode; and, ion exchangers filled in the diluting compartments,

5 wherein a thickness of the diluting compartments, operational electric voltage and/or current, and space velocity (SV) of flow are designed so that product water having pH higher than pH of feed water by 1.0 or more is obtained when the feed water having pH of equal to or less than 8.5 is treated without adding an alkaline agent.

10 2. An electrodeionization apparatus claimed in claim 1, wherein the diluting compartment has a thickness of equal to or more than 7mm, the operational voltage is 1 to 50V per cell, and the space velocity is 30 to 150 per hour.

15 3. An electrodeionization apparatus claimed in claim 1 or 2, wherein the ion exchanger is a mixture of an anion exchanger and a cation exchanger or the anion exchanger alone.

20 4. An electrodeionization apparatus as claimed in any one of claims 1 through 3, wherein hardness in the feed water can be removed by more than 50%.

25 5. An electrodeionization apparatus as claimed in any one of claims 1 through 4, wherein the feed water includes silica and/or boron.

30 6. An electrodeionization apparatus as claimed in any one of claims 1 through 4, wherein the rate (R_A/R_C) of electric resistance (R_A) of the anion exchange membrane and the electric resistance (R_C) of the cation exchange membrane is equal to or less than 0.8.

35 7. An electrodeionization apparatus claimed in any one of claims 1 through 6, wherein the whole space between the cathode and the cation membrane of the diluting compartments that is nearest to the cathode is designed for cathodic compartment,

40 wherein a cation exchange membrane is arranged between the anode and the anion exchange membrane of the diluting compartments that is nearest to the anode, wherein a concentrating compartments is designed between said cation exchange membrane and said diluting compartments that is nearest to the anode, and wherein an anodic compartment is designed between said cation exchange membrane and the anode.

45 8. An electrodeionization apparatus claimed in any one of claims 1 through 7, wherein the foremost electrodeionization apparatus is provided with the anion exchange membrane having an homogeneous thickness and the cation exchange membrane having an heterogeneous thickness.

50 9. An apparatus for producing purified water consists of two or more electrodeionization apparatuses connected so that water to be treated flows down therethrough, wherein the foremost electrodeionization apparatus is an electrodeionization apparatus claimed any one of claims 1 through 8.

55 10. An apparatus for producing pure water claimed in claim 9, wherein a diluting compartment of the second or later electrodeionization apparatus is thinner than the diluting compartments of the foremost electrodeionization apparatus.

60 11. An electrodeionization apparatus as claimed in claim 9 or 10, wherein said diluting compartments is divided into cells by a partition member, wherein at least a part of the partition member facing the cell is inclined relative to a normal flow direction of the water in the diluting compartment, and wherein at least inclined part of the partition member allows the water to pass, but prevents the ion exchanger to pass therethrough.

65 12. An apparatus for producing purified water claimed in any one of claims 9 through 11, wherein a pipe connecting the foremost electrodeionization apparatus and the second electrodeionization apparatus is provided with a pH meter,

wherein the operation of the foremost electrodeionization apparatus is controlled so that the measurement of pH measured by said pH meter is equal to or more than 8.5.

5 13. An apparatus for producing purified water claimed in any one of claims 9 through 12, wherein a pipe for discharging product water from the succeeding electrodeionization apparatus is provided with a meter for measuring the resistivity and/or the concentration of silica, and the electrodeionization apparatuses are controlled based on measurements of the meter.

10 14. An apparatus for producing purified water claimed in any one of claims 9 through 13, wherein a water recovery of the succeeding electrodeionization apparatus is equal to or more than 95%.

15 15. An apparatus for producing purified water claimed in any one of claims 9 through 14, wherein an ultraviolet-light irradiating apparatus is installed between the electrodeionization apparatuses.

20 16. An apparatus for producing purified water claimed in any one of claims 9 through 15, wherein a first reverse osmosis membrane apparatus is provided before the foremost electrodeionization apparatus and a second reverse osmosis membrane apparatus is provided between the electrodeionization apparatuses.

25 17. An apparatus for producing purified water claimed in any one of claims 9 through 16, wherein a reverse osmosis membrane apparatus is provided before the foremost electrodeionization apparatus and the product water of the reverse osmosis membrane apparatus is fed into and flows down through the electrodeionization apparatuses, and wherein the concentrated water of the preceding and/or succeeding electrodeionization apparatuses is fed back ahead of the reverse osmosis membrane apparatus.

30 18. An apparatus for producing purified water claimed in any one of claims 9 through 17, wherein a reverse osmosis membrane apparatus provided before the foremost electrodeionization apparatus, and the product water of reverse osmosis membrane apparatus is fed into the electrodeionization apparatuses, and wherein the concentrated water of the second or later electrodeionization apparatus is fed back to feeding pipe of the foremost, or later electrodeionization apparatus.

35 19. An electrodeionization apparatus in which a plurality of the cation exchange membrane and anion exchange membrane are arranged between a cathode and an anode to alternately form concentrating compartments and diluting compartments, and said diluting compartment is filled with an ion exchanger, wherein said electrodeionization apparatus has the diluting compartments having a thickness of equal to or more than 7 mm and the concentrating compartments having thickness of less than 7 mm, and feed water orderly flows through each diluting compartment in series.

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Fig. 1

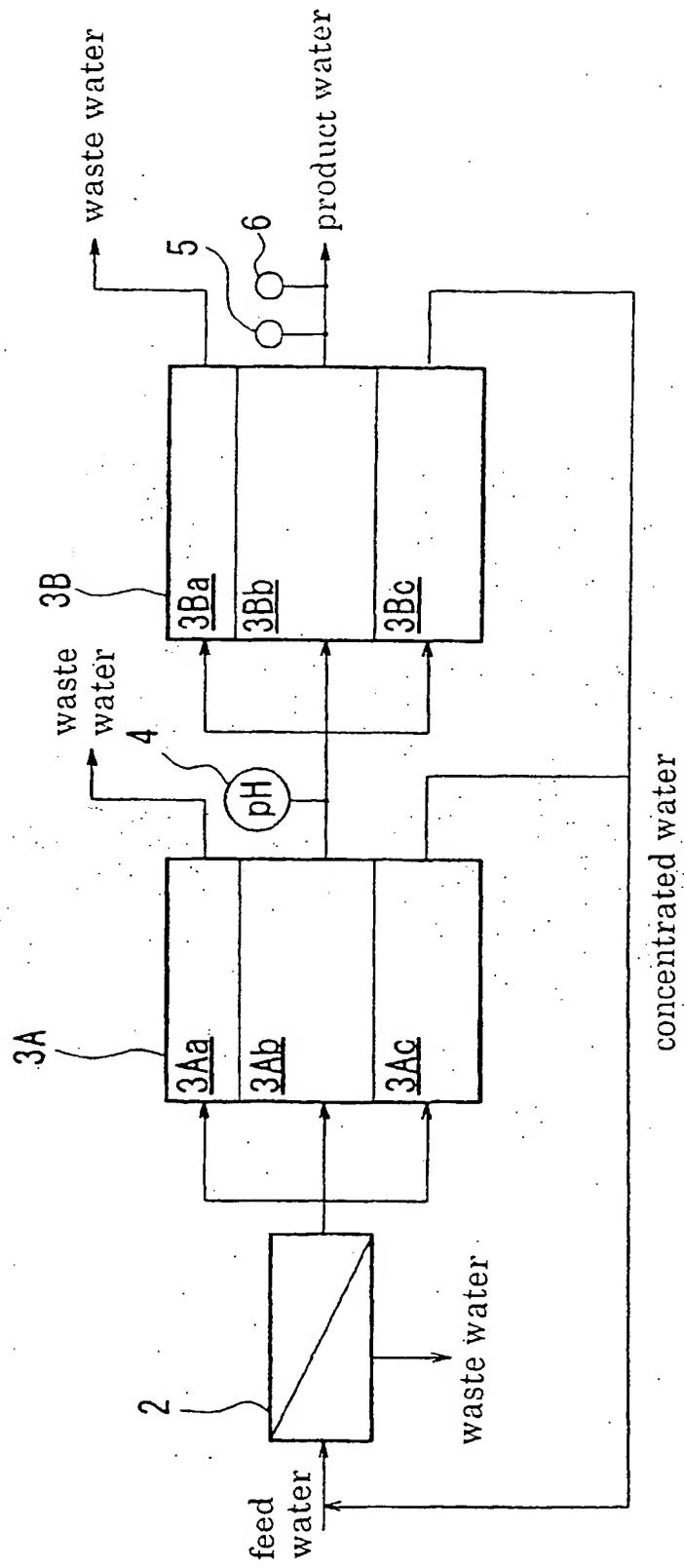


Fig. 2

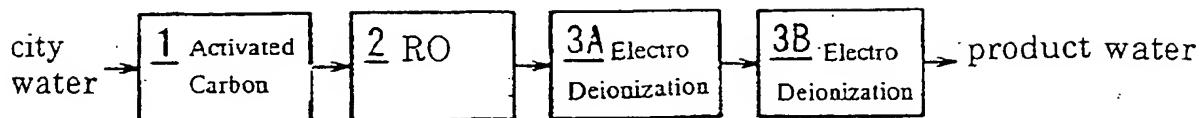


Fig. 3

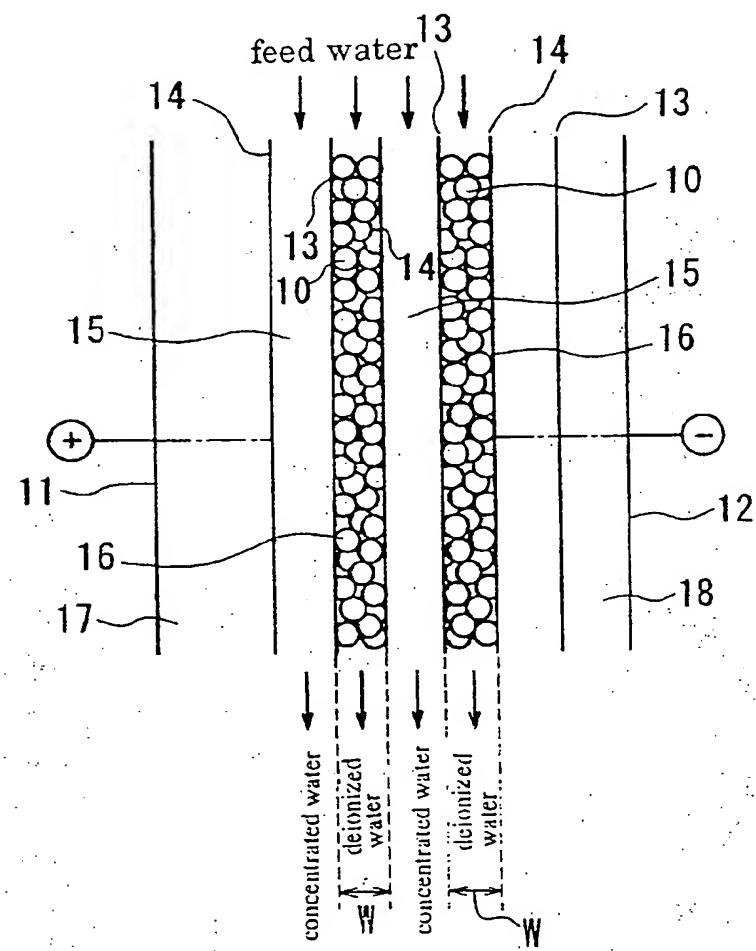


Fig. 4

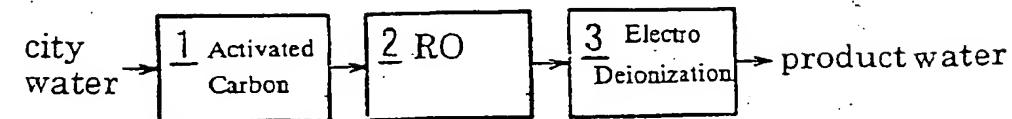


Fig. 5

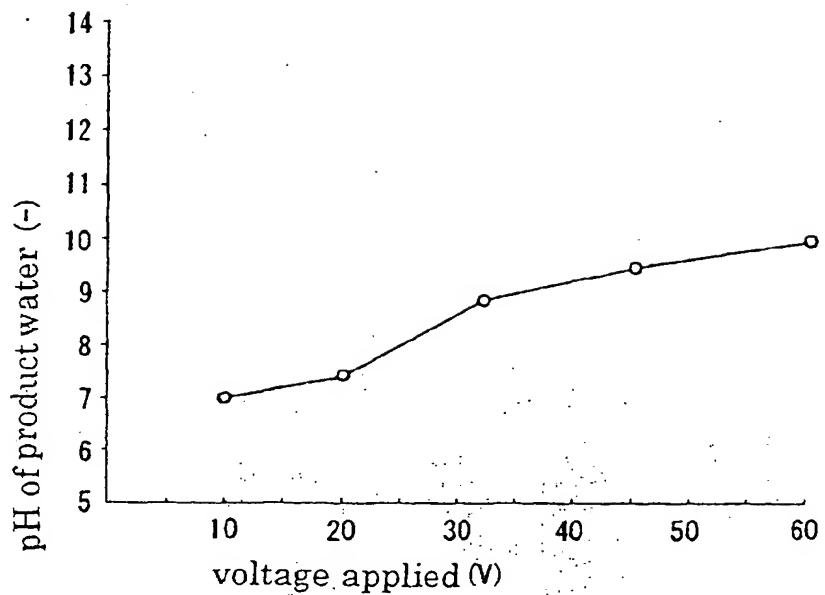


Fig. 6

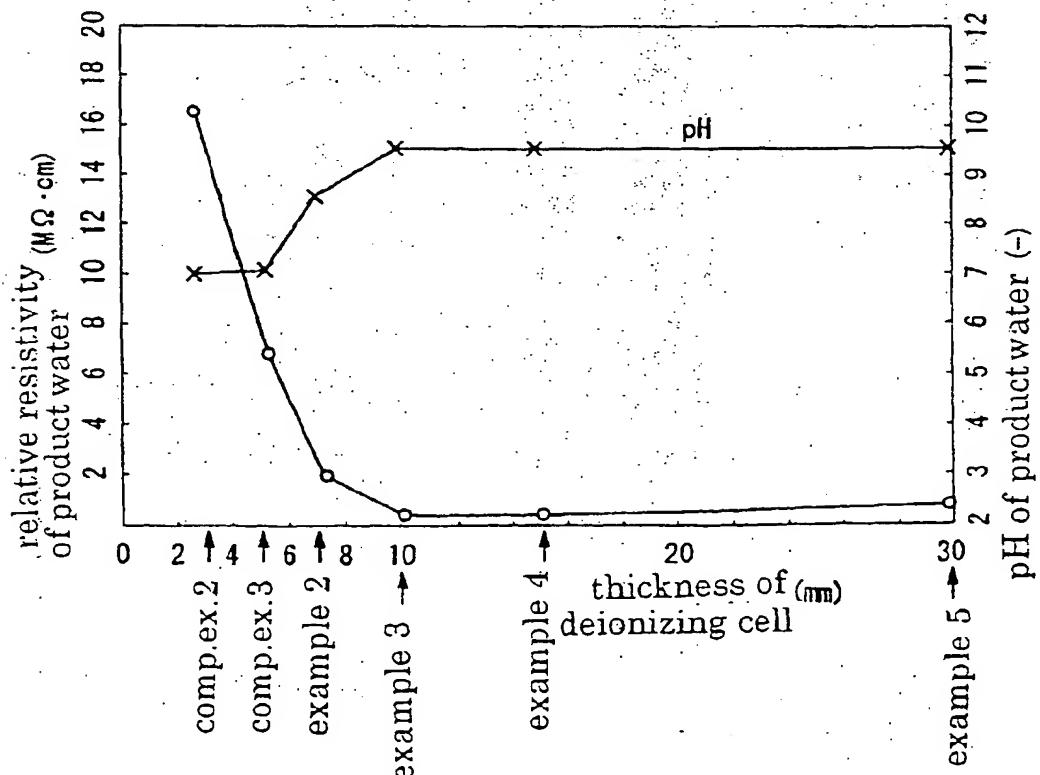


Fig. 7

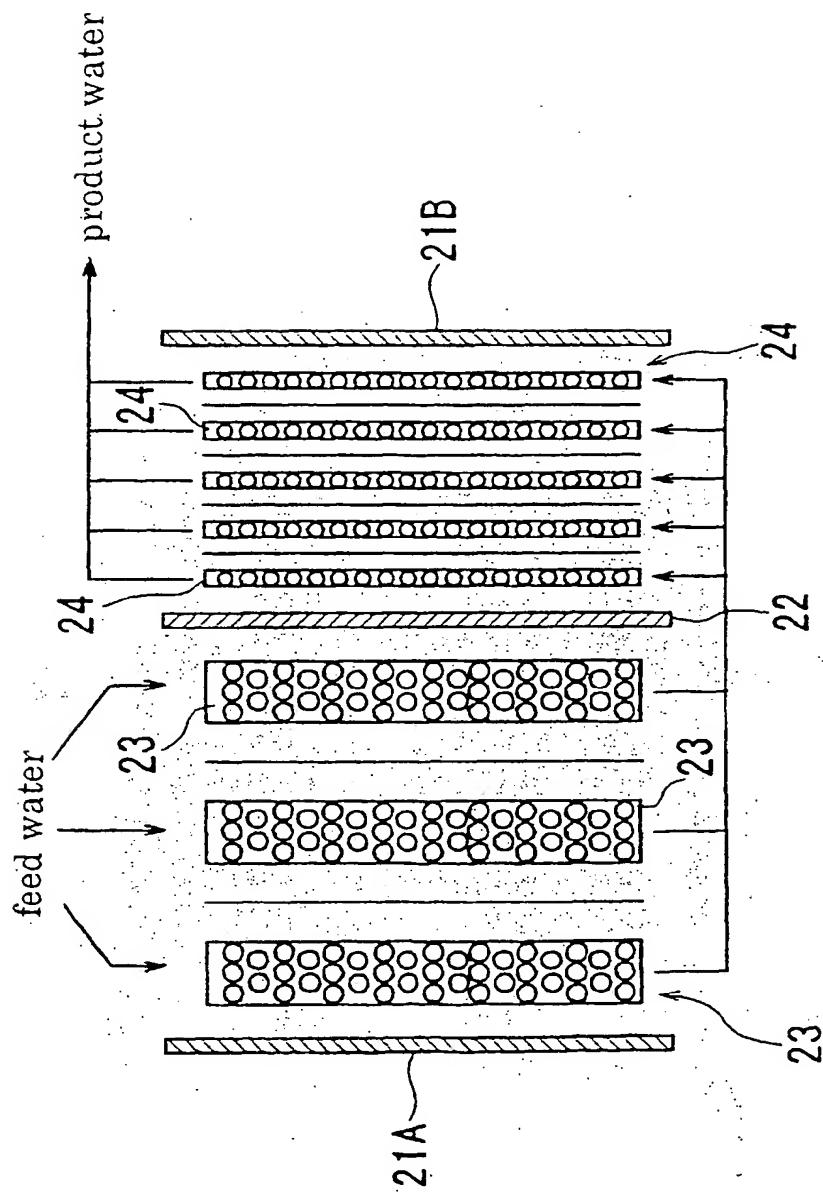


Fig. 8

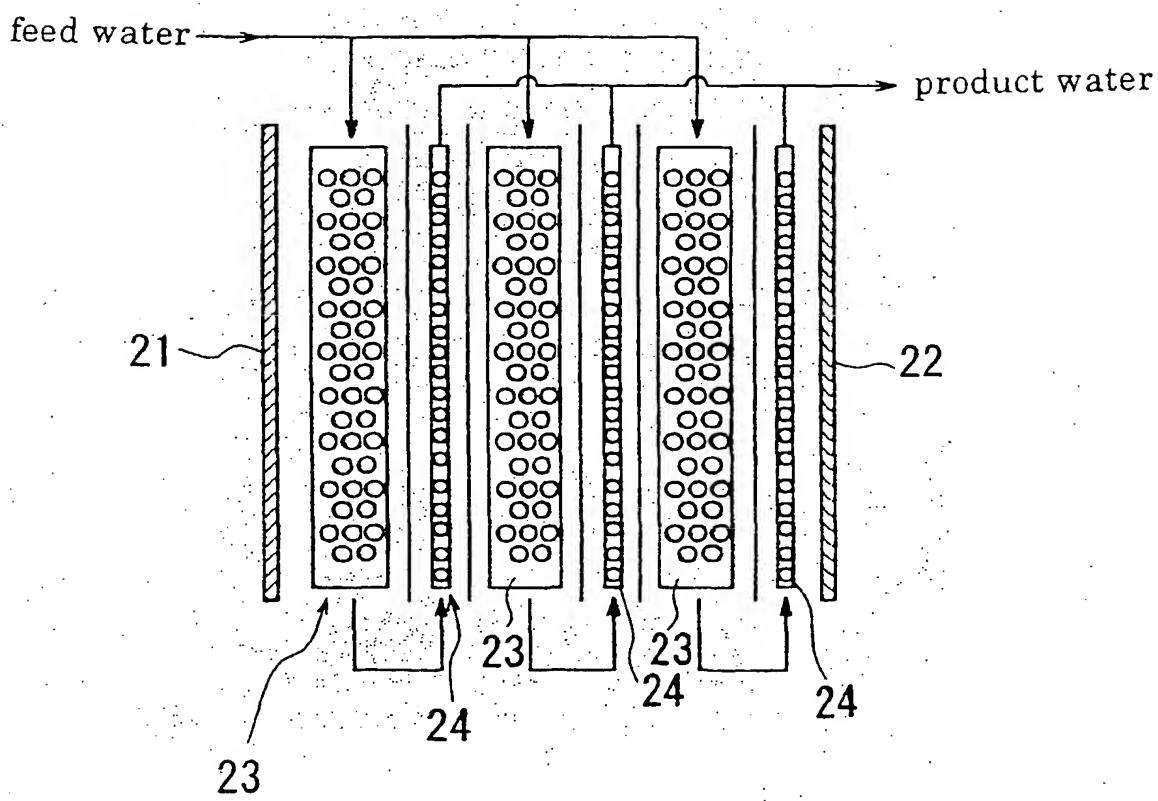


Fig. 9

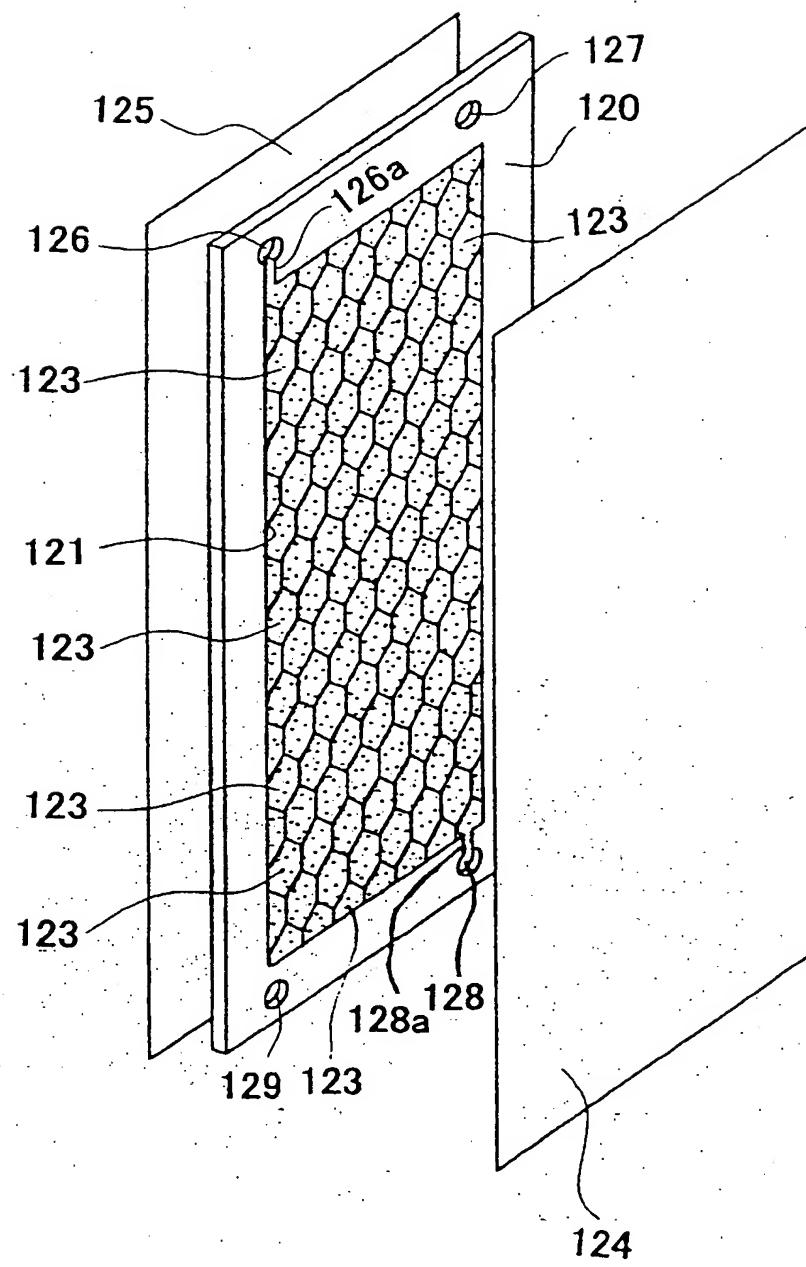


Fig. 10

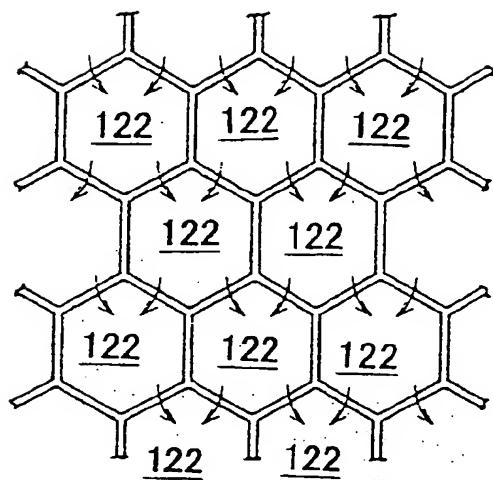


Fig. 11

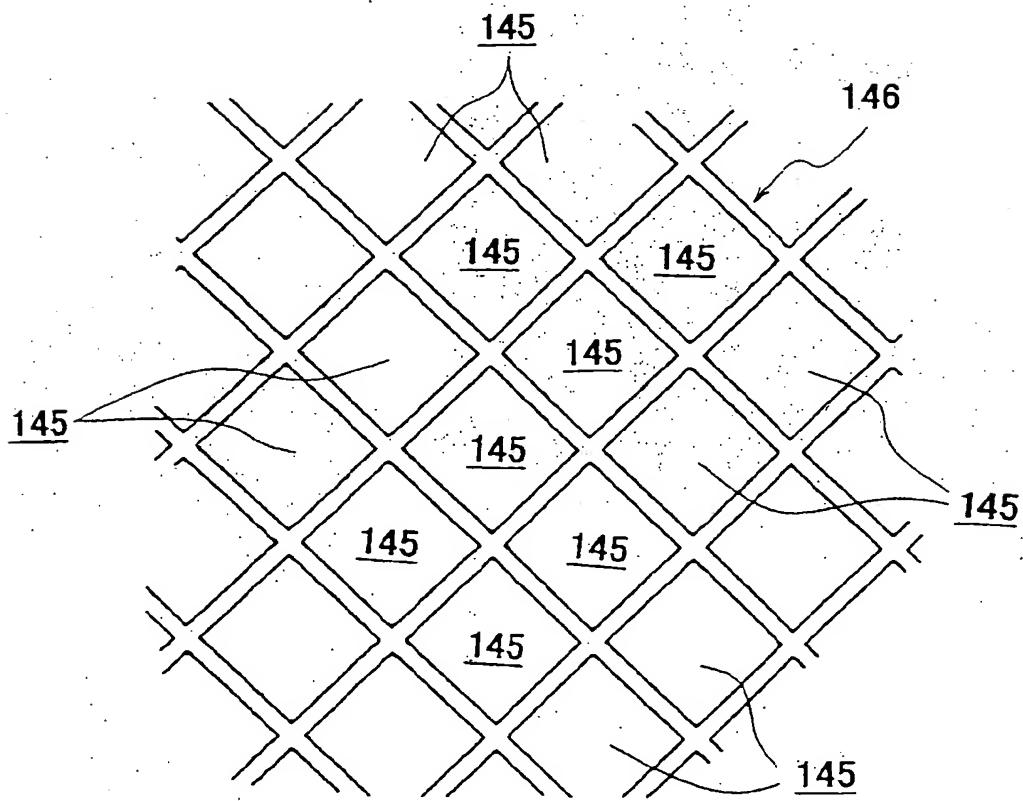


Fig. 12

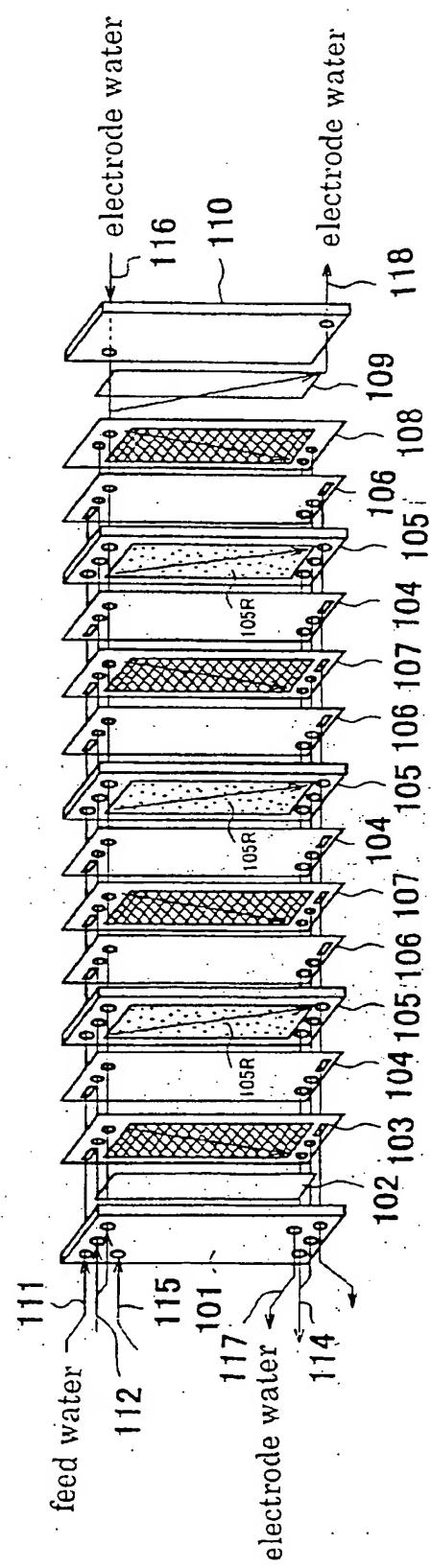


Fig. 13

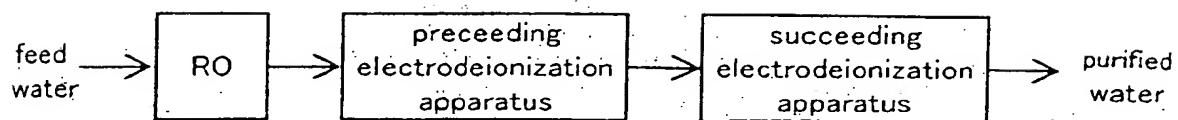


Fig.14

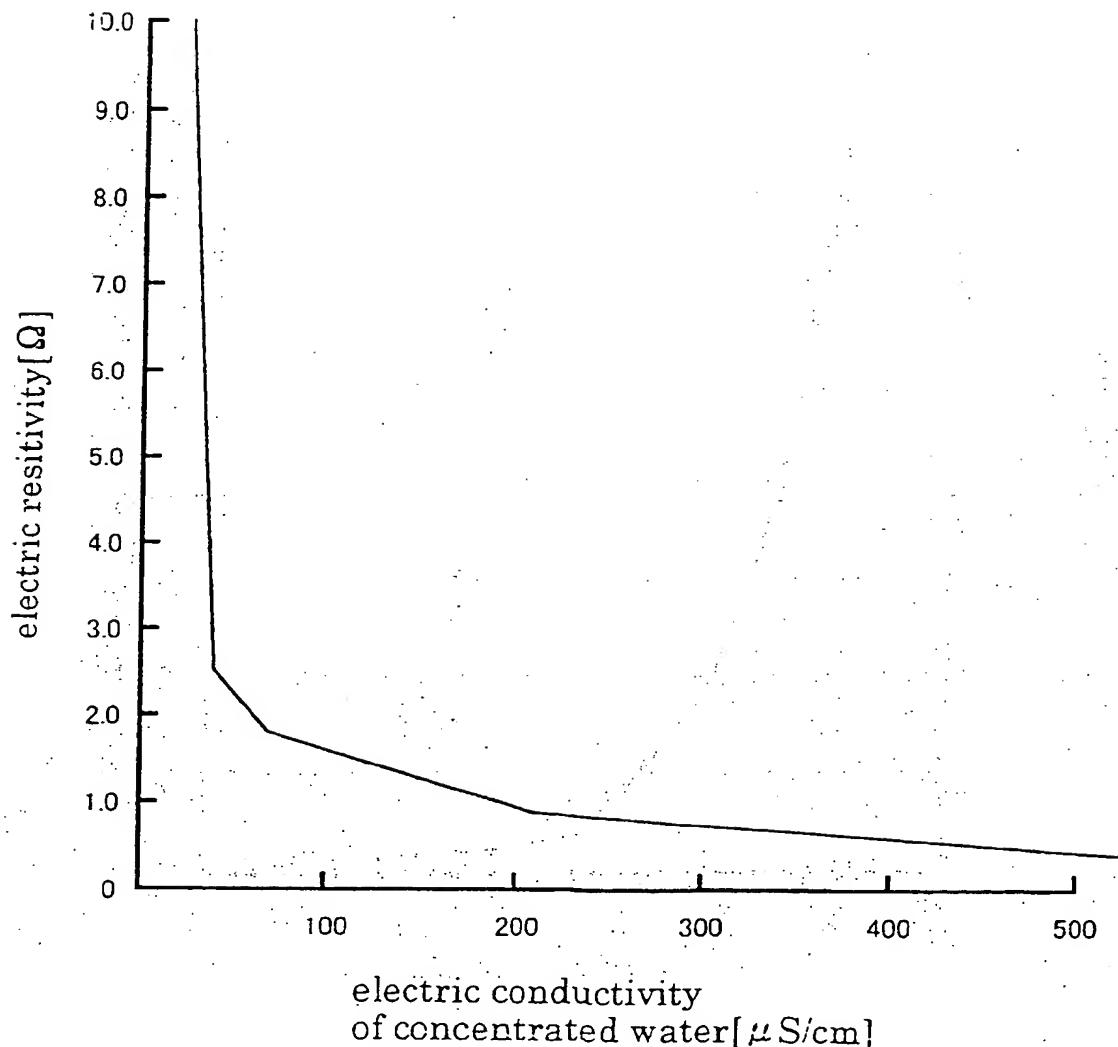
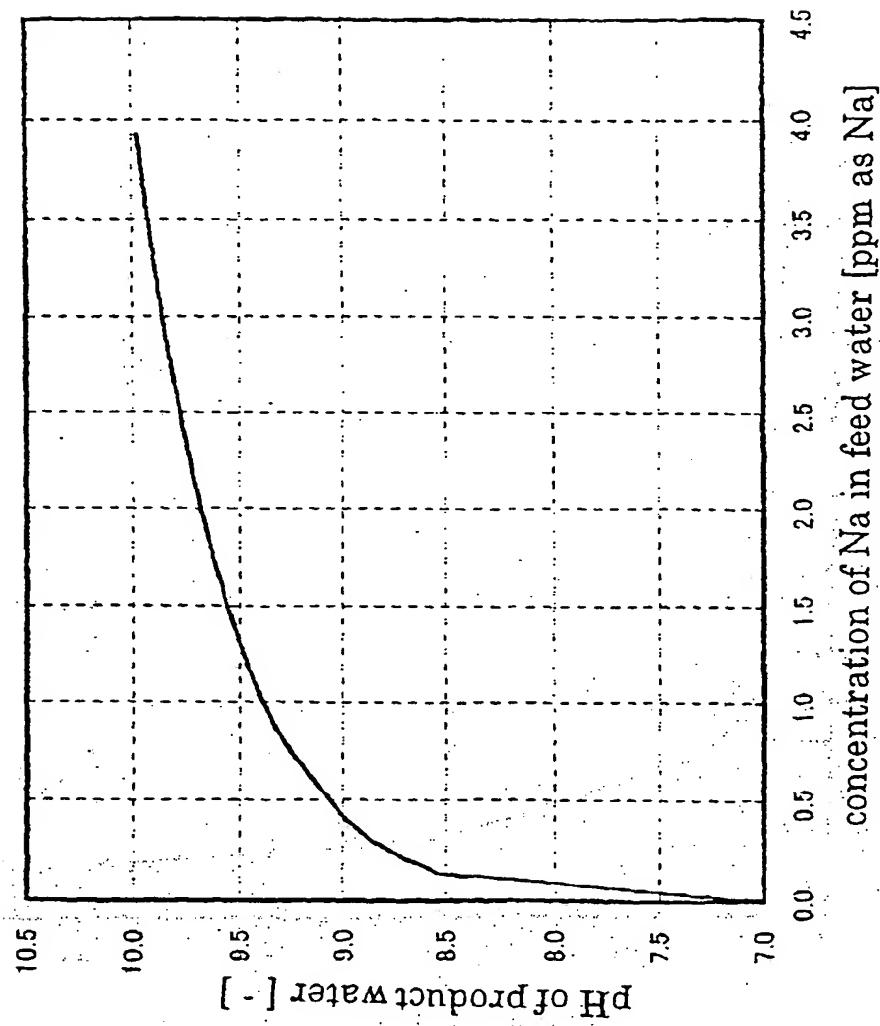


Fig. 15





(12)

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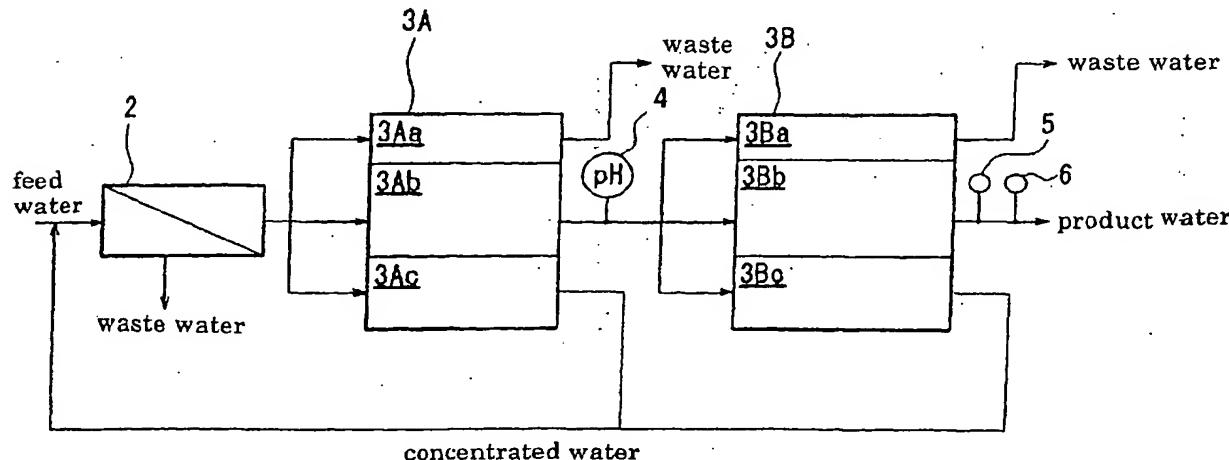
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(54) Electrodeionization apparatus and pure water producing apparatus

(57) The electrodeionization apparatus improves the removal rate of weakly - ionized species including silica and boron, and which species including silica and boron, and is useful for a primary pure water system and a reclaim system. The apparatus for producing purified water produces the product water of high quality including the resistivity of equal to or more than 18.0 MΩ · cm can be provided. The electrodeionization apparatus 3A has a plurality of cation exchange membrane and plurality of anion exchange membrane alternately arranged

between electrodes in such a manner as to alternately form diluting compartments and concentrating compartments. The diluting compartments are filled with an ion exchanger. The product water having pH exceeding pH of the feed water by 1.0 or more when the feed water having pH of equal to or less than 8.5 is treated without adding alkaline agents. The apparatus for producing purified water has plural electrodeionization apparatuses 3A, 3B connected each other so that the feed water flows through the electrodeionization apparatuses.

Fig. 1





European Patent
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EUROPEAN SEARCH REPORT

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EP 00 30 6837

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| Place of search | Date of completion of the search | Examiner | |
| THE HAGUE | 11 April 2003 | Liebig, T | |
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ON EUROPEAN PATENT APPLICATION NO.

EP 00 30 6837

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



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| (74) Agent: GANZI, Gary, C.; United States Filter Corporation, 75 Technology Drive, Lowell, MA 01851 (US). | | | |

(54) Title: ELECTRODEIONIZATION APPARATUS AND METHOD

(57) Abstract

The electrodeionization apparatus includes an ion-depleting compartment in which alternating layers of an electroactive media are positioned. One of the alternating layers is doped to provide a more balanced current distribution through the apparatus. The method involves providing reducing the difference in conductivity between the alternating layers positioned in the ion-depleting compartment by adding a dopant material to one of the layers.

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ELECTRODEIONIZATION APPARATUS AND METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to an electrodeionization apparatus and method and, more particularly, to an electrodeionization apparatus and method including electroactive media combinations that provide more uniform electric current distribution, degree of resin regeneration, and deionization performance.

10 2. Description of the Related Art

Electrodeionization (EDI) is a process that removes ionizable species from liquids using electrically active media and an electrical potential to influence ion transport. The electrically active media may function to alternately collect and discharge ionizable species, or to facilitate the transport of ions continuously by ionic or electronic substitution mechanisms. EDI devices 15 may comprise media of permanent or temporary charge, and may be operated batchwise, intermittently, or continuously. EDI devices may be operated to cause electrochemical reactions specifically designed to achieve or enhance performance, and may comprise electrically active membranes such as semipermeable ion exchange or bipolar membranes.

In continuous electrodeionization (CEDI), which includes processes such as continuous 20 deionization, filled cell electrodialysis, or electrodiagnosis (EDR), the ionic transport properties of the electrically active media are the primary sizing parameter. These processes are described, for example, by Kollsman in U.S. Patent No. 2,815,320; Pearson in U.S. Patent No. 2,794,777; Kressman in U.S. Patent No. 2,923,674; Parsi U.S. Patent Nos. 3,149,061 and 3,291,713; Korngold et al. in U.S. Patent No. 3,686,089; Davis in U.S. Patent No. 4,032,452; U.S. Patent No. 25 3,869,376; O'Hare in U.S. Patent No. 4,465,573; Kunz in U.S. Patent Nos. 4,636,296 and 4,687,561; and Giuffrida et al. in U.S. Patent No. 4,632,745. A typical CEDI device comprises alternating electroactive semipermeable, anion and cation ion-exchange membranes. The spaces between the membranes are configured to create liquid flow compartments with inlets and outlets. A transverse DC electrical field is imposed by an external power source using electrodes at the 30 bounds of the membranes and compartments. Often, electrolyte compartments are provided so that reaction products from the electrodes can be separated from the other flow compartments. Upon imposition of the electric field, ions in the liquid are attracted to their respective

counterelectrodes. The compartments bounded by the electroactive anion membrane facing the anode and the electroactive cation membrane facing the cathode become ionically depleted, and the compartments bounded by the electroactive cation membrane facing the cathode and the electroactive anion membrane facing the anode become ionically concentrated. The volume 5 within the ion-depleting compartments, and preferentially within the ion-concentrating compartments, is also comprised of electrically active media. In continuous deionization devices, the media may comprise intimately mixed anion and cation exchange resins. The ion-exchange media enhances the transport of ions within the compartments and can also participate as a substrate for controlled electrochemical reactions. The configuration is similar in EDR devices, 10 except that the media comprise separate, and sometimes alternating, layers of ion-exchange resin. In these devices, each layer is substantially comprised of resins of the same polarity (either anion or cation resin) and the liquid to be deionized flows sequentially through the layers.

Performance of CEDI may be limited by difficulty in obtaining the desired electrical current distribution with the device. Electroactive media of permanent charge may change their 15 electrical resistance properties in undesired ways depending on their ionic form. For example, in the ion substitution of sodium with hydrogen ion in EDR, most cation exchange resins will preferentially transport hydrogen ion over the desired transport of sodium ion. This results in electrical inefficiencies and, under certain circumstances, may cause pH shifts that are detrimental to valuable products within the liquid. In another example, a given electroactive media may be 20 desirable for transport properties, such as the Type II anion membrane and resins for continuous deionization and EDR, but may have the undesirable properties of catalyzing the ionization reaction of water to hydrogen and hydroxide ions.

NL 776,469 discloses an electrolytic deionization apparatus that includes separate strata of anion exchanger and cation exchanger.

25 WO97/46492 discloses an electrodeionization apparatus for improving the rate of silica removal in which nontreated water first passes through an anion-exchange layer followed by other ion-exchange materials.

Therefore, a need remains for an improved electrodeionization apparatus having improved 30 electric current distribution and deionization performance. Lastly, there is a need to provide improved methods of operation of an electrodeionization apparatus.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to an electrodeionization apparatus including an ion-depleting compartment having alternating layers of ion exchange resin material. At least one of the alternating layers includes a specialized electroactive media, which includes a Type I anion resin material. At least one of the alternating layers includes a doped cation exchange resin material.

In another aspect, the present invention is directed to an electrodeionization apparatus that includes an ion-depleting compartment with alternating layers of ion exchange resin material.

At least one of the alternating layers includes a specialized electroactive media. At least one of the alternating layers includes a doped cation exchange resin material. The cation resin material is doped with the specialized electroactive media. The specialized electroactive media includes about 60 percent of a Type I anion resin material.

In another aspect, the invention is directed to an electrodeionization apparatus that includes an ion-depleting compartment. The ion-depleting compartment includes alternating layers of ion exchange resin material. At least one layer includes a dopant material.

In yet another aspect, the invention is directed to a method for purifying a fluid in an electrodeionization apparatus. The method involves providing an electrodeionization apparatus having an ion-depleting compartment. The method also involves providing a first ion exchange resin material having a first conductivity value and a second ion exchange resin material having a second conductivity value different than the first. The difference between the first and second conductivity values may be reduced by adding a dopant material to at least one of the ion exchange resin materials. The first and second ion exchange resin materials are positioned in alternating layers in the ion-depleting compartment. A fluid stream is passed through the ion-depleting compartment, and an electric field is applied across the electrodeionization apparatus.

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BRIEF DESCRIPTION OF THE DRAWINGS

Preferred, non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying drawings, in which:

FIG. 1A is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating one configuration of alternating ion exchange resin material layers;

FIG. 1B is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating another configuration of alternating ion exchange resin material layers;

5 FIG. 1C is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating another configuration of alternating ion exchange resin material layers;

FIG. 1D is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating another configuration of alternating ion exchange resin material layers;

10 FIG. 1E is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating another configuration of alternating ion exchange resin material layers;

15 FIG. 1F is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating another configuration of alternating ion exchange resin material layers;

FIG. 2 is a schematic, cross-sectional view through an ion-depleting cell according to the present invention, illustrating an embodiment having substantially uniformly sized alternating ion exchange resin material layers; and

20 FIG. 3A is a schematic, cross-sectional view through an electrodeionization apparatus, illustrating the fluid and ion flow direction through ion-depleting, ion-concentrating, and electrolyte compartments;

FIG. 3B is a schematic, cross-sectional view through the electrodeionization apparatus of FIG. 3A, in which the ion-concentrating compartment is filled with alternating layers of ion exchange resin beads.

25 FIG. 3C is a schematic, cross-sectional view through the electrodeionization apparatus of FIG. 3A, in which the ion-concentrating compartment is filled with uniformly sized cation exchange resin beads.

DETAILED DESCRIPTION OF THE INVENTION

30 The present invention is directed to an electrodeionization apparatus and method that provide relatively high purity water and low electrical resistance by balancing the relative

conductivity of alternating layers of ion exchange resin material positioned in an ion-depleting compartment. The electrodeionization apparatus provides more uniform electric current distribution and deionization performance. An electrodeionization apparatus may be based on technologies such as continuous electrodeionization, electrodiagnosis, filled-cell electrodialysis, 5 electrochemical ion exchange, capacitive deionization, and the like. For purposes of the present invention, the electrodeionization apparatus is an EDI apparatus, such as those disclosed by Kunz, in U.S. Patent Nos. 4,636,296 and 4,687,561, both of which are incorporated herein by reference. The electrodeionization apparatus may be based on various configurations, such as a spiral design, a plate and frame design, and a circular design.

10 The method of the invention involves layering various types of electroactive media, each having a different conductivity value, in an ion-depleting compartment. The conductivity of the alternating layers of ion exchange resin material are balanced in order to provide more uniform current distribution and, ultimately, improved deionization performance. For purposes of the present invention, the terms "balanced" or "balancing," 15 mean a reduction in the difference in conductivity between two adjacent layers of electroactive media. One potential problem that may arise when the current distribution is unbalanced arises in instances where ion exchange resin materials are regenerated in situ by hydrogen and hydroxyl ions, as disclosed in U.S. Patent No. 5,858,191, which is incorporated herein by reference in its entirety. As disclosed, resin regeneration takes place where the 20 majority of current flows, and little or no regeneration takes place elsewhere. Therefore, the more highly conductive resin will be regenerated, while the less conductive resin will only be minimally regenerated, or not regenerated at all, leading to fouling of the less conductive resin. In the present invention, the current distribution of the apparatus is balanced by doping 25 at least one layer of the electroactive media. "Doped material," as used herein, means an electroactive media to which a dopant material has been added, for the purpose of adjusting the electrochemical characteristics of the electroactive media. The "dopant material" may be an inert or an electroactive media, preferably anion or cation exchange resin beads.

30 In conventional mixed bed, or mixtures of oppositely charged ion exchange resin materials, the mechanism of ion exchange is based on ionic transport. That is, ions of opposing charges are simultaneously transported from the deionization chamber in opposing directions. Such a mechanism does not take place in intimate mixtures of ion exchange

materials having the same charge, or mixtures of a single charge and an inert material. That is, they will never act as a mixed bed. In contrast, in the present invention, ionic substitution predominates, the majority of current flows in one direction, and the ions of interest are transported in a single direction. Thus, for purposes of the present invention, an electroactive material may be considered "doped" up to the point at which the transport of ions in both directions is the predominant mechanism, i.e. until the electroactive material begins to function as a mixed bed. Those of skill in the art will recognize that mixed beds in which 5 ionic transport ceases or is minimized and in which ionic substitution predominates may be considered doped materials for purposes of the present invention. Those of skill in the art will 10 also recognize that the maximum amount of dopant that may be added to an electroactive media before ionic transport predominates will vary according to the materials used.

According to the invention, alternating layers of anion exchange resin beads and cation 15 exchange resin beads may be positioned in the ion-depleting compartment, in any sequence. Examples of such electroactive media are used throughout the application, and are described 20 in more detail below. That is, either anion exchange resin beads or cation exchange resin beads may be positioned in the first, or topmost, layer of the ion-depleting compartment. Moreover, either, or both layers of the beads may be doped. For ease of manufacturing, it is 25 preferred that the layers are doped using beads from the alternating layers. For example, a layer of anion exchange resin beads is preferably doped with cation exchange resin beads of a type used in an adjacent layer. Conversely, a layer of cation exchange resin beads is preferably doped with anion exchange resin beads of a type used in an adjacent layer.

For ease of illustration, all embodiments and examples described herein are with 25 reference to ion exchange resin beads. However, it should be understood that beads are used solely for the purposes of illustration, and that the invention encompasses any other type of electroactive media.

In FIGS. 1A-1F, varying schematic, cross-sectional views of an ion-depleting compartment 10 according to the present invention are shown. According to the 30 embodiments, alternating layers, or beds, of ion exchange resin material are positioned in the ion-depleting compartment 10 in a central space formed between an anion-permeable membrane 26 and a cation-permeable membrane 24. The central space, or inter-membrane spacing, may be varied depending on the desired purity of the product water. The inter-

membrane spacing may be adjusted depending on the desired product water purity, and is typically greater than about 1/16 inch. In one application requiring very high purity water, for example, having a resistivity of between about 16 megohms to about 18 megohms, it has been found that the preferred inter-membrane spacing is in the range of about 1/16 inch to about 3/16 inch, and most preferably about 1/8 inch. In another application with a lower purity requirement, for example, having a resistivity of between about 9 megohms to about 12 megohms, it has been found that the preferred inter-membrane spacing is in the range of about 1/4 inch to about 1/2 inch, most preferably about 3/8 inch.

At least one layer of ion exchange resin material 28 and ion exchange resin material 30 is required in the ion-depleting compartment of the present invention, although more may be used. The number of layers in the ion-depleting compartment may be determined, in part, by the height of the module frame. The thickness of the layers may vary depending, in part, on the inter-membrane spacing. In practice, the layer thickness, which is also known as the bed height, is limited by the minimum thickness required to reduce shifting and undesired mixing of the alternating layers of resins during use. In some instances, it may be necessary to vary the thickness of the alternating layers, however, it is preferred that the individual layers in the ion-depleting compartment have substantially the same thickness. Although as few as two alternating resin layers may be used in the ion-depleting compartment, up to eight or more resin layers of equal or different heights are typically used.

20 In one aspect of the invention illustrated in FIGS. 1A-1C, the first, or topmost layer, is
preferably an anion exchange resin material 28, and the second layer is preferably a cation
exchange resin material 30. In one embodiment illustrated in FIG. 1A, the first layer of anion
exchange resin material 28 is preferably doped with a dopant material 38, while the second
layer of cation exchange resin beads 30 is preferably undoped. Conversely, in another
25 embodiment illustrated in FIG. 1B, the first layer of anion exchange resin material 28 is
preferably undoped, while the second layer of cation exchange resin material 30 is preferably
doped with a dopant material 38. In another embodiment illustrated in FIG. 1C, both the first
anion exchange resin material layer 28 and the second cation exchange resin material layer 30
are preferably doped with dopant material 38.

30 FIGS. 1D-1F illustrate another aspect of the invention, in which the first, or topmost layer in the ion-depleting compartment is a cation exchange resin material 30, and the second

layer is an anion exchange resin material 28. In one embodiment illustrated in FIG. 1D, the first cation exchange resin material layer 30 is preferably doped with a dopant material 38, while the second anion resin material layer 28 is preferably undoped. Conversely, in another embodiment illustrated in FIG. 1E, the first cation exchange resin material layer 30 is 5 preferably undoped, while the second anion exchange resin material 28 is preferably doped with a dopant material 38. In another embodiment illustrated in FIG. 1F, both the first cation exchange resin material layer 30 and the second anion exchange resin material layer 28 are preferably doped with dopant material 38. When either, or both, of the alternating layers are doped, they may be doped with the same dopant material, or they may be doped with different 10 dopant materials. Preferably, when either, or both, of the alternating layers of ion exchange resin material 28 and 30 are doped, they are doped with less than about 50 percent, more preferably less than about 40 percent, more preferably less than about 30 percent, more preferably less than about 20 percent, and more preferably still less than about 10 percent, of a dopant material, by volume of the layer to be doped. As noted above, the dopant material 15 may be an inert or an electroactive media, preferably anion or cation exchange resin beads.

The optimum ratios of dopant material to ion exchange resin beads may vary based, in part, on the inter-membrane spacing, the thickness of the layers, the composition of both the dopant material and the ion exchange resin beads to be doped, the size and uniformity of the beads, and the functional groups in the surface regions of the beads. It will be readily 20 apparent to those of skill in the art that as the difference in conductivity between two resins increases, the amount of resin required to effect a change in the conductivity of the ion exchange resin material may increase. In some instances, it may be desirable to minimize the amount of dopant material in order to prevent or minimize changes in the properties of the ion exchange resin material to which it is added.

25 Also in any of the embodiments disclosed herein, the remaining ion-concentrating and electrode compartments may be filled with conventional ion exchange resin material, which may be alternated as in the ion-depleting compartment. These compartments may also be filled with an inert material, such as, but not limited to, polypropylene. Alternatively, the remaining ion-concentrating and electrode compartments may include an inert structure, such as a screen or netting positioned therein. It should be recognized that any type of electroactive 30 media may be used in the ion-concentrating and electrode compartments, including, but not

limited to cation exchange resin material, Type I anion exchange resin material, Type II anion exchange resin material, weak base anion exchange resin material, synthetic materials, including carbon, zeolite resin material, inert materials, and mixtures thereof, which are described in more detail below. An inert material may be formed from any material which 5 does not conduct current or take part in water dissociation, while permitting fluid flow to pass through the ion-depleting cell. However, deionization performance will vary depending on the choice of resin material used in such compartments. It will be apparent to those of ordinary skill in the art that optimum conductivity and deionization performance will be obtained by using any type of material that achieves the highest conductivity or lowest 10 resistivity across the apparatus, in combination with the best deionization performance. Therefore, a simple test for selecting the best material to use is to determine which type of material provides the highest conductivity, or lowest resistivity, through the module. Those of ordinary skill in the art may accomplish this through routine experimentation. The arrangement of alternating layers in the ion-concentrating compartment, in addition to the 15 alternating layers in the ion-depleting compartment, would eliminate a direct path of current flow from electrode to electrode through the material with a higher conductivity and enhance the uniformity of the electric current distribution throughout the module.

Generally, in any of the embodiments disclosed herein, it is advantageous to use the smallest possible bead diameter in order to maximize the available surface area of the 20 electroactive media. However, one of ordinary skill in the art will recognize that smaller beads result in increased pressure drops across the ion-depleting chamber, which decreases operating efficiency. Therefore, the minimum size of the beads is limited by the maximum acceptable pressure drop across the ion-depleting compartment, which may vary depending on the apparatus design. One of ordinary skill in the art would be able to select the size of the 25 beads through routine experimentation, using the deionization performance as the determining factor.

Also according to any of the embodiments disclosed herein, deionization performance may be improved further by using substantially uniformly sized ion exchange resin beads in the alternating layers positioned in the ion-depleting compartment. "Substantially uniform," 30 as used herein with reference to the bead size, means that 90 percent of the beads are within +/- 10 percent of the mean bead size, and that the relative average size of one ionic form of

beads to a second ionic form of beads in a mixture of beads is at least 0.8. When beads are packed within a chamber, the packing density and size of voids between the beads will vary depending on the volume to be filled, as well as the size and uniformity of the beads. When non-uniform beads are used, the beads are typically packed more tightly in some areas, 5 resulting in a variety of void sizes or volumes, with the void volumes varying within the chamber. Consequently, current may travel through the more tightly packed areas, resulting in non-uniform current distribution. In contrast, when uniform beads are used, the beads are packed more uniformly throughout the chamber volume, resulting in more uniformly sized voids throughout the chamber volume, and ultimately providing more uniform current 10 distribution. It should be understood that as the ratio of substantially uniform beads to non-uniform beads increases, greater increases in deionization performance are achieved. That is, it is not necessary to use 100 percent substantially uniform beads in order to achieve benefits in deionization performance.

Commercially available examples of electroactive media in the form of ion exchange 15 resin materials include, but are not limited to, DOWEX™ MARATHON™ series resins, (e.g., DOWEX™ MARATHON™ C cation resins, MARATHON™ A and MARATHON™ A2 anion resins), DOWEX™ WBA (weak base) anion resins, DOWEX™ 11 Type I anion resin, DOWEX™ SAR anion resin (e.g., DOWEX™ SAR Type II anion resins). Other 20 commercially available examples of ion exchange resins include the AMBERJET™ series resins (trademark of Rohm & Haas Corporation, Philadelphia, PA), such as, for example, AMBERJET™ 4600 Type II anion resins. DOWEX™ MARATHON™ C cation resin is a gel-type strong acid cation exchange resin with sulfonic acid functional groups. DOWEX™ MARATHON™ A is a gel-type strong base Type I anion exchange resin with quaternary ammonium functional groups. DOWEX™ MARATHON™ A2 is a gel-type strong base 25 Type II anion exchange resin with dimethyl ethanolamine functional groups. One particularly preferred example of ion exchange resin material is the DOWEX™ MARATHON™ MSA and MSC series resins. DOWEX™ MARATHON™ MSA is a high capacity, macro porous type I strong base anion exchange resin having functional groups and mean particle sizes ranging from 590 to 690 microns. The DOWEX™ MARATHON™ MSC ion exchange resin 30 is a high capacity macro porous strong acid count ion exchange resin having sulfonic acid

11 functional groups and uniform particle sizes ranging from 450 to 570 microns. Both the DOWEX™ MARATHON™ MSA and MSC ion exchange resin are characterized by high water content, high degree of cross-linking, therefore are advantageous for removing silica, and are also advantageous for CEDI applications.

5 Other commercially available examples of ion exchange resin materials having substantially uniform beads include DOWEX™ MONOSPHERE™ 650C cation resin (Dow Chemical Company), having an average bead size of about 650 microns, and DOWEX™ MONOSPHERE™ 550A Type I anion resin (Dow Chemical Company), having an average bead size of about 550 microns.

10 Other types of electroactive media include, but are not limited to, zeolite resin material, synthetic activated carbons, hypercrosslinked sorbent resins such as PUROLITE™ HYPERSOL-MACRONET™ sorbent resins (trademarks of Purolite Company, Bala Cynwyd, PA), synthetic carbonaceous adsorbents, such as AMBERSORB™ carbonaceous adsorbents (trademark of Rohm & Haas Corporation) and G-BAC™ adsorbents (trademark of Kureha Chemical Industry Co., Ltd., Japan), polymeric adsorbent resin beads that are prepared by alkyline bridging haloalkylated, porogen-modified, cross-linked copolymer beads, having microporosities in the range of about 0.2 and 0.5 cm³/cm, mesoporosities of at least about 0.5 cm³/g, and total porosity of at least about 1.5 cm³/g as disclosed, for example, by Stringfield, in U.S. Patent No. 5,460,725, and catalytic carbon as disclosed, for example, by Hayden, in 15 U.S. Patent No. 5,444,031, and Matviya et al., in U.S. Patent No. 5,356,849.

20 In FIG. 2, a schematic, cross-sectional view of a preferred ion-depleting compartment 10 according to the present invention is shown. In the present embodiment, alternating layers, or beds, of ion exchange resin material 28 and 30 are positioned within the ion-depleting compartment 10 in a central space formed between an anion-permeable membrane 26 and a cation-permeable membrane 24. In the present embodiment, four alternating ion exchange 25 resin layers are positioned in the ion-depleting compartment. Also in the present embodiment, the inter-membrane spacing is preferably in the range of about 1/4 inch to about 3/8 inch, and the layer thickness is between about 2 inches to about 4 inches.

20 In the present embodiment, the ion-depleting compartment 10 preferably includes a layer of anion exchange resin beads 28, which are alternated with a layer of cation exchange

resin beads 30, within the central space formed between the anion-permeable membrane 26 and the cation-permeable membrane 24 of ion-depleting compartment 10. Preferably, the size of the anion and cation resin beads used in the present embodiment ranges from between about 200 μm and about 800 μm ; more preferably, between about 400 and about 700 μm ; and more preferably between about 550 μm and about 650 μm . Preferably, the anion exchange resin beads are a specialized electroactive media, such as described in U.S. Patent No. 5,868,915, which is hereby incorporated by reference. For ease of manufacturing, it is preferred that the cation exchange resin beads are doped with the same anion exchange resin material as used in the alternating layers. One such preferred specialized electroactive medium is an anion exchange resin material that includes between about 1 percent and about 20 percent; more preferably, between about 5 percent and about 15 percent; and, most preferably, about 10 percent, by volume, of Type II or weak base anion exchange resin material, with the remainder comprising Type I anion exchange resin material. In a preferred embodiment, the anion exchange resin material layers include about 90 percent Type I anion exchange resin material and about 10 percent Type II anion exchange resin material, and the cation exchange resin layers are doped with about 22.5 percent of the Type I anion exchange resin material and 2.5 percent Type II anion exchange resin material, by volume of the layer. When uniformly sized resin beads are used, the cation exchange resin material layers preferably include about 36 percent Type I anion exchange resin material and about 4 percent Type II anion exchange resin material, by volume of the layer.

The layer of doped cation exchange resin material 30 in the ion-depleting compartment 10 preferably includes between about 50 percent and about 99 percent, by volume, of cation exchange resin material, which is doped with between about 1 percent and about 50 percent, by volume, of anion exchange resin material; more preferably, between about 60 percent and about 90 percent, by volume, of a cation exchange resin material, which is doped with between 10 percent and about 40 percent, by volume, of anion exchange resin material; and more preferably, between about 70 percent and about 80 percent, by volume, of a cation exchange resin material, which is doped with between about 20 percent and about 30 percent of anion exchange resin material, by volume, based on the volume of the layer. That is, the doped cation exchange resin layers 30, according to this aspect of the invention, preferably include between about 50 percent and about 99 percent cation exchange resin

material, which are doped with between about 0.1 percent and about 5 percent of Type II anion exchange resin material, and between about 0.9 percent and about 45 percent Type I anion exchange resin material; more preferably, between about 60 percent and about 90 percent cation exchange resin material, which is doped with between about 1 percent and about 4 percent of Type II anion exchange resin material, and between about 9 percent and about 36 percent Type I anion exchange resin material; more preferably, about 70 percent to about 80 percent cation exchange resin material, which is doped with between about 2 percent and about 3 percent of Type II anion exchange resin material, and between about 18 percent and about 27 percent Type I anion exchange resin material, by volume, based on the volume 10 of the layer

In any of the disclosed embodiments, as the amount of Type II or weak base anion exchange resin material in the specialized electroactive media increases, the ability of the media to dissociate in solutions along the entire pH range and to split and exchange neutral salts decreases due to the decrease in volume of Type I anion exchange resin material in the 15 layer. Therefore, when using the previously described specialized electroactive media, as in the present embodiment, balancing the conductivity of the alternating layers of cation exchange resin materials and anion exchange resin materials, by decreasing the conductivity of the layers of cation exchange resin beads, so as not to affect the properties of the anion exchange resin beads used in the layers, has been found to be more preferable than doping the 20 layers of anion exchange resin beads.

FIG. 3A illustrates schematic, cross-sectional views of the fluid and ion flow paths through one preferred EDI apparatus of the invention. In FIG. 3A, the EDI module 12 includes ion-depleting compartments 10 and an ion-concentrating compartment 14 positioned between the ion-depleting compartments. The ion-depleting compartments 10 are bordered by an anolyte compartment 16 and a catholyte compartment 18. Typically, end blocks are positioned adjacent to end plates (not shown) to house an anode 20 and a cathode 22 in their respective compartments. Cation-selective membranes 24 and anion-selective membranes 26 are typically sealed to the periphery of both sides of the compartments. Alternating layers, or beds, of ion exchange resin material 28 and 30 are positioned within the ion-depleting compartment 10 in a central space formed between the cation-permeable membrane 24 and the anion-permeable membrane 26. The ion-depleting compartment 10 is illustrated, as in

FIG. 2, with four alternating ion exchange resin layers positioned therein, and with an inter-membrane spacing in the range of about 1/4 inch to about 1/2, more preferably about 3/8 inch, and a layer thickness or bed height of between about 2 inches to about 4 inches. In any of the disclosed embodiments, the ion-concentrating and electrode compartments may be empty or may be filled with other types of electroactive media. The electrode compartments and the ion-concentrating compartments of the EDI apparatus illustrated in FIG. 3A do not contain any electroactive media positioned therein. However, if desired, one or both of the electrode and ion-concentrating compartments may contain any of the electroactive media described herein.

10 Alternatively, as illustrated in FIG. 3B, which is a schematic, cross-sectional view through the electrodeionization apparatus of FIG. 3A, the ion-concentrating compartment is filled with alternating layers of ion exchange resin beads, as in the ion-depleting compartment. In FIG. 3B, the first and third layers of the ion-concentrating compartment are doped cation resin material, and the second and fourth layers are the specialized electroactive media described previously.

15 FIG. 3C is a schematic, cross-sectional view of a preferred electrodeionization apparatus, as illustrated in FIG. 3A, in which the ion-concentrating compartment is filled with uniformly sized cation exchange resin beads. Preferably, the ion-concentrating compartment is filled with a strong acid cation exchange resin material, preferably including 20 sulfonic acid functional groups. One such commercially available cation exchange resin material is DOWEX™ MONOSPHERE™ 650C (not shown), which includes uniformly sized resin beads.

25 In operation, a liquid to be purified 32, which may be a reverse osmosis product stream, typically having dissolved cationic and anionic components, is fed through the ion-depleting compartments 10, wherein the anionic components are attracted to the anion exchange resin 28 and the cationic components are attracted to the cation exchange resin beads 30. An electric field is then applied across the anode 20 and cathode 22 at the opposite ends of the module. The electric current passes perpendicularly to the fluid flow such that the dissolved cationic and anionic components migrate from the alternating ion exchange resin 30 layers in the direction of their corresponding electrode. Cationic components migrate through the cation-selective membrane 24 into the adjacent ion-concentrating compartment 14. An

anion-selective membrane on the opposite side of the ion-concentrating compartment prevents further migration, thereby trapping the cationic components in the ion-concentrating compartment. The process for the anionic components is similar but occurs in the opposite direction; anionic components migrate through the anion-selective membrane 26 into the ion-concentrating compartment 14 and a cation-selective membrane 24 on the other side of the ion-concentrating compartment prevents further migration to trap the anionic components in the ion-concentrating compartment. Ionic components are depleted from the ion-depleting compartments 10 and increased in the ion-concentrating compartments 14, forming a high purity product stream 34 and a concentrate stream 36.

10 The electrodeionization apparatus may be operated under conditions of chemical solute, or temperature cycling, and/or electrical field polarity cycling or reversal, as described in co-pending application 08/717,781.

15 The present invention will be further illustrated by the following examples, which are intended to be illustrative in nature and are not to be considered as limiting the scope of the invention.

EXAMPLES

The following examples were performed in a electrodeionization apparatus that included an ion-depleting compartment, and ion-concentrating compartment, and anolyte compartment, and a catholyte compartment. Each compartment was bounded by a resin sheet membrane, with 20 an inter-membrane spacing of about 3/8 inch. Alternating layers of ion exchange resin material were positioned in the ion-depleting compartments of the electrodeionization apparatus. Each ion-depleting compartment contained four alternating layers, beginning with a layer of anion exchange resin beads. The bed height, or layer thickness, ranged from about 2 inches to about 4 inches.

25 A reverse osmosis permeate stream, having a conductivity of about 3.0 to about 5.0 μ S/cm, at a temperature of between about 18°C and about 20°C, was used as the feed in each example. The modules were operated at a flow rate of about 1.6 lpm/cell-pair, with a product recovery of about 85 percent. The applied DC amperage to the module was 1.5 A, which corresponded to a current density of about 3 mA/cm².

16
EXAMPLE I

The effectiveness of an electrodeionization apparatus in which the conductivity of the ion-exchange materials in the ion-depleting compartments was balanced according to the present invention, was compared to an electrodeionization apparatus in which the conductivity of the ion-exchange materials in the ion-depleting compartment was not balanced.

Two twelve-cell-pair modules were used for the experiments (Modules A and B). The ratios of the materials used in each module are outlined below in Table 1. Each ion-depleting compartment contained four alternating layers, beginning with a layer of substantially uniform anion exchange resin beads. The anion exchange resin beads used in the alternating layers of each ion-depleting compartment contained 90 percent of substantially uniform Type I anion exchange resin beads (DOWEX™ MONOSPHERE™ 550A) and 10 percent of uniform Type II anion exchange resin beads (AMBERJET 4600). The layer of cation exchange resin beads used in the alternating layers of Module A were undoped strong acid cation exchange resin beads (DOWEX™ MONOSPHERE™ 650C), also having a substantially uniform bead size.

In Module B, the cation layers were doped in order to balance the conductivity of the alternating layers. The layers of cation exchange resin beads used in the alternating layers of Module B were doped using about 40 percent of the anion exchange resin beads used in the layers of both Module A and Module B. (i.e., the layers included 60 percent of the uniform strong acid cation resin (DOWEX™ MONOSPHERE™ 650C), 36 percent of the uniform Type I anion exchange resin beads (DOWEX™ MONOSPHERE™ 550A), and 4 percent of a Type II anion exchange resin beads (AMBERJET 4600).

TABLE 1

| Module A Layers | Type I Anion Exchange Resin Beads | Type II Anion Exchange Resin Beads | Cation Exchange Resin Beads |
|--------------------|--------------------------------------|---------------------------------------|--------------------------------|
| First | 90 % uniform | 10 % uniform | 0 % |
| Second | 0 % | 0 % | 100 % uniform |
| Third | 90 % uniform | 10 % uniform | 0 % |

| | | | |
|------------------------|--|---|------------------------------------|
| Fourth | 0 % | 0 % | 100 % uniform |
| Module B Layers | Type I Anion Exchange Resin Beads | Type II Anion Exchange Resin Beads | Cation Exchange Resin Beads |
| First | 90 % uniform | 10 % uniform | 0 % |
| Second | 36 % uniform | 4 % uniform | 60 % uniform |
| Third | 90 % uniform | 10 % uniform | 0 % |
| Fourth | 36 % uniform | 4 % uniform | 60 % uniform |

The performance of Module A and Module B was evaluated with regard to the product resistivity, product pH, and electrical resistance, recorded after reaching a steady state of operation. As shown below in Table 2, the electrical resistance of Module A was lower than 5 Module B, the pH of the product from Module A was slightly acidic, and the product resistivity of Module A was lower than Module B. When the cation exchange resin beads were not doped, as in Module A, the conductivity of the alternating layers was less balanced, and more of the current traveled through the relatively highly conductive cation resin layers. In contrast, when the cation exchange resin beads were doped, as in Module B, current was more evenly distributed 10 through the module, resulting in improved deionization performance.

TABLE 2

| Module | Product Resistivity (MΩ-cm) | Product pH | Electrical Resistance (Ω) |
|--------|-----------------------------|------------|---------------------------|
| A | 0.16 | < 7.0 | 8.53 |
| B | 15.4 | ~ 7.0 | 28.3 |

EXAMPLE II

The effectiveness of the electrodeionization apparatus of the present invention was evaluated with respect to an electrodeionization apparatus utilizing non-uniform anion exchange resin beads.

Three six-cell-pair modules were used for the experiments (Modules A, B, and C). Each ion-depleting compartment contained four alternating layers, beginning with a layer of anion exchange resin beads. The anion exchange resin beads used in the alternating layers of each ion-depleting compartment contained 90 percent of non-uniform Type I anion exchange resin beads (DOWEX™ 11, non-uniform grade) and 10 percent of uniform Type II anion exchange resin beads (AMBERJET 4600). The cation resin beads used in the alternating layers of Module A were substantially uniform undoped strong acid cation exchange resin beads (DOWEX™ MONOSPHERE™ 650C). Thus, the only difference between Module A of the present example and Module A of Example I is that the majority of beads used in Example I were substantially uniform. Modules B and C included alternating layers of doped cation exchange resin beads, according to the present invention, in order to balance the conductivity of the alternating layers. The doped cation exchange resin beads used in the alternating layers of Module B contained 60 percent of the uniform strong acid cation resin (DOWEX™ MONOSPHERE™ 650C) and 40 percent of the same anion exchange resin beads used in the alternating layers of Modules A, B, and C ((i.e. 60 percent uniform strong acid cation resin beads (DOWEX™ MONOSPHERE™ 650C), 36 percent of the non-uniform Type I anion exchange resin beads (DOWEX™ 11, non-uniform grade), and 4 percent uniform Type II anion exchange resin beads (AMBERJET 4600)). Module C contained the same type of resins as Module B, but the doping ratio of the cation resin beads was less. Accordingly, the layers of cation exchange resin beads used in the alternating layers of Module C contained the same uniform strong acid cation resin beads (DOWEX™ MONOSPHERE™ 650C), doped with about 25 percent of the same anion exchange resin beads in the alternating layers of the Module ((i.e. 75 percent uniform strong acid cation resin beads (DOWEX™ MONOSPHERE™ 650C), 22.5 percent of a non-uniform Type I anion exchange resin beads (DOWEX™ 11, non-uniform grade), and 2.5 percent of a uniform Type II anion exchange resin beads (AMBERJET 4600)).

TABLE 3

| Module A Layers | Type I Anion Exchange Resin Beads | Type II Anion Exchange Resin Beads | Cation Exchange Resin Beads |
|--------------------|--------------------------------------|---------------------------------------|--------------------------------|
| First | 90 % non-uniform | 10 % uniform | 0 % |
| Second | 0 % | 0 % | 100 % uniform |
| Third | 90 % non-uniform | 10 % uniform | 0 % |
| Fourth | 0 % | 0 % | 100 % uniform |
| Module B Layers | Type I Anion Exchange Resin Beads | Type II Anion Exchange Resin Beads | Cation Exchange Resin Beads |
| First | 90 % non-uniform | 10 % uniform | 0 % |
| Second | 36 % non-uniform | 4 % uniform | 60 % uniform |
| Third | 90 % non-uniform | 10 % uniform | 0 % |
| Fourth | 36 % non-uniform | 4 % uniform | 60 % uniform |
| Module C Layers | Type I Anion Exchange Resin Beads | Type II Anion Exchange Resin Beads | Cation Exchange Resin Beads |
| First | 90 % non-uniform | 10 % uniform | 0 % |
| Second | 22.5 % non-uniform | 2.5 % uniform | 75 % uniform |
| Third | 90 % non-uniform | 10 % uniform | 0 % |
| Fourth | 22.5 % non-uniform | 2.5 % uniform | 75 % uniform |

The performance of Modules A, B, and C was evaluated with regard to the product resistivity, product pH, and electrical resistance, recorded after reaching a steady state of operation. As shown below in Table 4, Module A, in which the conductivity of the alternating layers was not balanced, had the lowest product resistivity and electrical resistance, with slightly acidic product water. Module B, which had the same ratios of resins as used in Module B of the previous Example, but used non-uniform resins, had very low product resistivity, the highest

electrical resistance, and slightly basic product water. Module C had the best deionization performance, with very high product resistivity, relatively high electrical resistance, and a neutral pH.

5

TABLE 4

| Module | Product Resistivity (MΩ-cm) | Product pH | Electrical Resistance (Ω) |
|--------|--------------------------------|------------|------------------------------|
| A | 0.12 | < 7.0 | 8.5 |
| B | 3.42 | > 7.0 | 16.5 |
| C | 16.3 | ~ 7.0 | 14.8 |

The results of the modules that were balanced according to the present invention in both Experiment I and II are summarized and compared below in Table 5. The only difference between Module B of Experiments I and II is the uniformity of the material used to dope the 10 cation exchange resin beads, i.e., the majority of anion exchange resin beads used in Experiment I were substantially uniform and the majority of anion exchange resin beads resins used in Experiment II were non-uniform. Comparing the results of the two Modules shows that as a result of the substitution of the non-uniform beads, the product resistivity dropped, and the pH of the product became slightly basic, indicating less cation removal. Therefore, it may be 15 concluded that a 4 to 5 fold increase in product resistivity is achieved when the conductivity of the alternating layer is balanced by doping with substantially uniform beads. The only difference between Modules B and C of Experiment II is the ratio of dopant material in the layers of cation exchange resin beads. In Module B, the ratio was 40 percent dopant material to 60 percent cation exchange resin beads, and in Module C, the ratio was 25 percent dopant material to 75 percent 20 cation exchange resin beads. As a result of the 15 percent reduction in dopant material contained in the layers of cation exchange resin beads, a 4 to 5 fold increase in product resistivity and slightly lower electrical resistance was produced in Module C. The results of the experiments show that both uniform and non-uniform dopant materials may be used to balance the conductivity of alternating layers, and that a greater amount of dopant material may be required 25 when uniform beads are used.

TABLE 5

| | Module B (Experiment I) | Module B (Experiment II) | Module C (Experiment II) |
|---|----------------------------|-----------------------------|-----------------------------|
| Percent Dopant material in Cation Exchange Resin layer | 40% | 40% | 25% |
| Bead Characteristics | Uniform | Non-uniform | Non-uniform |
| Product Resistivity (MΩ-cm) | 15.4 | 3.4 | 16.3 |
| Product pH | ~ 7.0 | > 7.0 | ~ 7.0 |
| Electrical Resistance (Ω) | 28.3 | 16.5 | 14.8 |

Although particular embodiments of the invention have been described in detail for purposes of illustration, various changes and modifications may be made without departing from the scope and spirit of the invention. All combinations and permutations of the electroactive media and operational methods are available for practice in various liquid deionization applications as the need arises. For example, the electrodeionization apparatus and method of the present invention can be applied to processes that are presently not practically feasible due to lack of scaling and fouling resistance, temperature resistance, chemical resistance, or electrical efficiency. Typical applications would be the purification and softening of relatively untreated municipal water, relatively untreated well water and brackish water, and water containing foulants such as polyelectrolytes, tannins, lignins, fulvic acid, and other polar or weakly ionized or large ionized organic compounds, foulants such as iron, sulfide, phosphates, silicates, and other multivalent ions. Other applications would be in the treatment and processing of foods and beverages, sugars and various sugar fractionations and chemical modifications, starches, milk and milk by-products, by-products from cheese manufacture such as whey, purification and fractionation of proteins, products of various fermentation processes such as alcoholic beverages, pharmaceutical products and the like, processes in the chemical, pharmaceutical, food and beverage industries requiring ion substitutions in the presence of foulants and chemical oxidants, mixed solutes in low level radioactive waste streams, waste water streams containing heavy metals and organic compounds, and liquids in industries such as the food and beverage, chemical, pharmaceutical, power, and chemical industries where operation at elevated temperatures are

required, or where sterilization or sanitization by heat or chemical oxidants is required.

Accordingly, the invention is not to be limited except as by the appended claims.

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What is claimed is:

CLAIMS

1. An electrodeionization apparatus, comprising:
an ion-depleting compartment comprising alternating layers of ion exchange resin material;
5 wherein at least one of said alternating layers comprises a specialized electroactive media, and said specialized electroactive media comprises a Type I anion exchange resin material; and
at least one of said alternating layers comprises a doped cation exchange resin material.
- 10 2. The electrodeionization apparatus of claim 1, wherein said specialized electroactive media further comprises a material selected from the group consisting of Type II anion exchange resin material, weak base anion exchange resin material, and mixtures thereof.
- 15 3. The electrodeionization apparatus of claim 2, wherein said specialized electroactive media comprises about 90 percent of said Type I anion exchange resin material.
4. The electrodeionization apparatus of claim 3, wherein said ion-depleting compartment comprises four alternating layers of said ion exchange resin material.
- 20 5. The electrodeionization apparatus of claim 4, wherein a first and third layer of said four alternating layers of ion exchange resin material comprise said specialized electroactive media.
- 25 6. The electrodeionization apparatus of claim 4, wherein a second and a fourth layer of said four alternating layers of ion exchange resin material comprise of said specialized electroactive media.
- 30 7. The electrodeionization apparatus of claim 5, wherein a second and a fourth layer of said four alternating layers of ion exchange resin material comprise said doped cation exchange resin material.

8. The electrodeionization apparatus of claim 6, wherein a first and a third layer of said four alternating layers of ion exchange resin material comprise said doped cation exchange resin material.

5

9. The electrodeionization apparatus of claim 7, wherein said doped cation exchange resin material comprises about 40 percent of said specialized electroactive media.

10. The electrodeionization apparatus of claim 8, wherein said doped cation exchange resin material comprises about 40 percent of said specialized electroactive media.

11. The electrodeionization apparatus of claim 7, wherein said doped cation exchange resin material comprises about 25 percent of said specialized electroactive media.

15 12. The electrodeionization apparatus of claim 8, wherein said doped cation exchange resin material comprises about 25 percent of said specialized electroactive media.

20 13. The electrodeionization apparatus of any of the preceding claims, wherein said ion-depleting compartment includes opposing membranes spaced apart by at least about 1/16 inch.

14. The electrodeionization apparatus of claim 13, wherein said ion-depleting compartment includes opposing membranes spaced apart by about 1/16 to about 1/4 inches.

25 15. The electrodeionization apparatus of claim 13, wherein said ion-depleting compartment includes opposing membranes, and said inter-membrane spacing is about 1/4 to about 1/2 inches.

30 16. The electrodeionization apparatus of claim 13, wherein said alternating layers each comprise ion exchange resin beads of substantially uniform size.

17. The electrodeionization apparatus of claim 14, wherein said alternating layers each comprise ion exchange resin beads of substantially uniform size.

18. The electrodeionization apparatus of claim 15, wherein said alternating layers each 5 comprise ion exchange resin beads of substantially uniform size.

19. The electrodeionization apparatus of claim 16, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

10 20. The electrodeionization apparatus of claim 17, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

21. The electrodeionization apparatus of claim 18, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

15 22. The electrodeionization apparatus of claim 21, wherein said layers have a thickness of between about 2 inches to about 4 inches.

23. An electrodeionization apparatus, comprising:
20 an ion-depleting compartment comprising alternating layers of ion exchange resin material;
at least one of said alternating layers comprising a specialized electroactive media;
at least one of said alternating layers comprising a doped cation exchange resin material, wherein said dopant material comprises said specialized electroactive media;
25 wherein said specialized electroactive media comprises at least about 60 percent of a Type I anion exchange resin material.

24. The electrodeionization apparatus of claim 23, wherein said specialized electroactive media further comprises a material selected from the group consisting of Type II 30 anion exchange resin material, weak base anion exchange resin material, and mixtures thereof.

25. The electrodeionization apparatus of claim 24, wherein a first layer in said ion-depleting compartment is said doped cation exchange resin material.

5 26. The electrodeionization apparatus of claim 24, wherein a second layer in said ion-depleting compartment is said doped cation exchange resin material.

27. The electrodeionization apparatus of claim 25, wherein said doped cation exchange resin material comprises about 40 percent of said specialized electroactive media.

10 28. The electrodeionization apparatus of claim 26, wherein said doped cation exchange resin material comprises about 40 percent of said specialized electroactive media.

29. The electrodeionization apparatus of claim 25, wherein said doped cation exchange resin material comprises about 25 percent of said specialized electroactive media.

15 30. The electrodeionization apparatus of claim 26, wherein said doped cation exchange resin material comprises about 25 percent of said specialized electroactive media.

20 31. The electrodeionization apparatus of any of claims 23-30, wherein said ion-depleting compartment is bounded by opposing membranes spaced apart by at least about 1/16 inch.

25 32. The electrodeionization apparatus of any of claim 31, wherein said ion-depleting compartment is bounded by opposing membranes spaced apart by about 1/16 inch to about 1/4 inch.

33. The electrodeionization apparatus of claim 31, wherein said ion-depleting compartment is bounded by opposing membranes, and said inter-membrane spacing is about 1/4 inch to about 1/2 inch.

34. The electrodeionization apparatus of claim 31, wherein said alternating layers comprise ion exchange resin beads of substantially uniform size.

5 35. The electrodeionization apparatus of claim 32, wherein said alternating layers comprise ion exchange resin beads of substantially uniform size.

36. The electrodeionization apparatus of claim 33, wherein said alternating layers comprise ion exchange resin beads of substantially uniform size.

10 37. The electrodeionization apparatus of claim 34, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

38. The electrodeionization apparatus of claim 35, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

15 39. The electrodeionization apparatus of claim 36, wherein said substantially uniform size beads have a mean diameter of about 500 μm to about 800 μm .

20 40. The electrodeionization apparatus of claim 39, wherein said layers comprise a thickness of between about 2 inches to about 4 inches.

25 41. An electrodeionization apparatus, comprising:
an ion-depleting compartment comprising alternating layers of ion exchange resin material, wherein at least one layer comprises a dopant material.

42. The electrodeionization apparatus of claim 41, wherein said at least one layer comprises less than about 50 percent, by volume, of said dopant material.

30 43. The electrodeionization apparatus of claim 42, wherein said at least one layer comprises less than about 40 percent, by volume, of said dopant material.

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44. The electrodeionization apparatus of claim 43, wherein said at least one layer comprises less than about 30 percent, by volume, of said dopant material.

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45. The electrodeionization apparatus of claim 44, wherein said at least one layer comprises less than about 20 percent, by volume, of said dopant material.

46. The electrodeionization apparatus of claim 45, wherein said at least one layer comprises less than about 10 percent, by volume, of said dopant material.

10
47. The electrodeionization apparatus of any of claims 41-46, wherein said dopant material is selected from the group consisting of cation exchange resin material, Type I anion exchange resin material, Type II anion exchange resin material, weak base anion resin material, zeolite resin material, synthetic activated carbon, hypercrosslinked sorbent resins, synthetic carbonaceous adsorbents, polymeric adsorbent resin beads, catalytic carbon, inert materials, and mixtures thereof.

15
48. The electrodeionization apparatus of claim 47, wherein said dopant material is selected from the group consisting of Type II anion exchange resin material, weak base anion exchange resin material, and mixtures thereof.

20
49. The electrodeionization apparatus of claim 41, wherein at least two adjacent ion exchange resin layers comprise a dopant material.

50. The electrodeionization apparatus of claim 49, wherein said at least two adjacent 25 layers each comprise less than about 50 percent, by volume, of a dopant material.

51. The electrodeionization apparatus of claim 50, wherein said at least two adjacent layers each comprise less than about 40 percent, by volume, of a dopant material.

30
52. The electrodeionization apparatus of claim 51, wherein said at least two adjacent layers each comprise less than about 30 percent, by volume, of a dopant material.

53. The electrodeionization apparatus of claim 52, wherein said at least two adjacent layers each comprise less than about 20 percent, by volume, of a dopant material.

5 54. The electrodeionization apparatus of claim 53, wherein said at least two adjacent layers each comprise less than about 10 percent, by volume, of a dopant material.

10 55. The electrodeionization apparatus of any of claims 49-54, wherein said dopant material is selected from the group consisting of cation exchange resin material, Type I anion exchange resin material, Type II anion exchange resin material, weak base anion resin material, zeolite resin material, synthetic activated carbon, hypercrosslinked sorbent resins, synthetic carbonaceous adsorbents, polymeric adsorbent resin beads, catalytic carbon, inert materials, and mixtures thereof.

15 56. The electrodeionization apparatus of claim 55, wherein at least one of said two layers is doped with a dopant material selected from the group consisting of Type II anion exchange resin material, weak base anion exchange resin material, and mixtures thereof.

20 57. The electrodeionization apparatus of claim 41, wherein said alternating layers include uniformly sized resin beads.

58. The electrodeionization apparatus of claim 41, wherein said ion-depleting compartment includes opposing ion-permeable membranes spaced apart by about 1/4 inch to about 1/2 inch.

25

30 59. A method for purifying a fluid in an electrodeionization apparatus, comprising: providing an electrodeionization apparatus having an ion-depleting compartment; providing a first ion exchange resin material having a first conductivity value and a second ion exchange resin material having a second conductivity value different than the first; reducing the difference between said first and second conductivity values by adding a dopant material to one of said first or second ion exchange resin materials;

positioning said first and second ion exchange resin materials in alternating layers in said ion-depleting compartment;

passing a fluid stream through said ion-depleting compartment; and
applying an electric field across said electrodeionization apparatus.

5

60. The method of claim 59, wherein a first layer in said ion-depleting compartment is an anion exchange resin material.

10 61. The method of claim 60, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by at least about 1/16 inch.

62. The method of claim 61, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by about 1/16 to about 1/4 inch.

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63. The method of claim 62, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by about 1/4 to about 1/2 inch.

20

64. The method of claim 63, further comprising providing said alternating layers at a thickness of about 2 to about 4 inches.

65. The method of claim 59, further comprising providing uniformly sized first and second ion exchange resin materials.

25

66. The method of claim 65, further comprising providing said uniformly sized ion exchange materials with a mean diameter of about 500 μm to about 800 μm .

30 67. The method of claim 59, wherein a first layer in said ion-depleting compartment is a cation exchange resin material.

68. The method of claim 59, further comprising reversing the polarity of the applied electric field in order to remove fouling from said ion exchange material.

5 69. The method of claim 68, further comprising providing said alternating layers at a thickness of about 2 to about 4 inches.

70. The method of claim 69, further comprising providing uniformly sized first and second ion exchange resin materials.

10 71. The method of claim 69, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by at least about 1/16 inch.

15 72. The method of claim 71, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by about 1/16 to about 1/4 inch.

73. The method of claim 71, further comprising providing said ion-depleting compartment with opposing ion permeable membranes spaced apart by about 1/4 to about 1/2 inch.

20 74. The method of claim 70, further comprising providing said uniformly sized ion exchange materials with a mean diameter of about 500 μm to about 800 μm .

25 75. The electrodeionization apparatus of claim 1, further comprising an ion-concentrating compartment.

76. The electrodeionization apparatus of claim 75, wherein said ion-concentrating compartment comprises an ion exchange resin material.

30 77. The electrodeionization apparatus of claim 76, wherein said ion-exchange resin material comprises a cation exchange resin material.

78. The electrodeionization apparatus of claim 76, wherein said ion-exchange resin material comprises an inert screen.

5 79. The electrodeionization apparatus of claim 76, wherein said ion-concentrating compartment comprises alternating layers of ion exchange resin material.

10 80. The electrodeionization apparatus of claim 78, wherein at least one of said alternating layers is doped.

15 81. An electrodeionization apparatus, comprising:
an ion-depleting compartment comprising alternating layers of ion exchange resin material, each layer having substantially the same thickness, wherein at least one layer comprises a dopant material.

20 82. An electrodeionization apparatus, comprising:
an ion-depleting compartment comprising alternating layers of ion exchange resin material, wherein a first layer comprises a doped cation exchange resin material, said apparatus constructed and arranged to provide a flow of water to be introduced into said first layer.

25 83. An electrodeionization apparatus, comprising:
an ion-depleting compartment constructed and arranged to provide ionic substitution in said ion-depleting compartment, and substantially uniform current distribution throughout said apparatus,
said compartment including alternating layers of ion exchange resin material, at least one layer including a dopant material.

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FIG. 1C

ANION
CATION
DOPANT

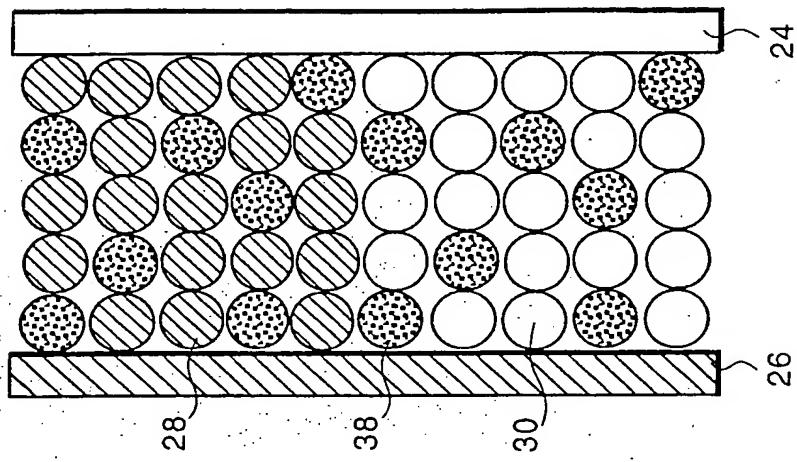


FIG. 1B

ANION
CATION
DOPANT

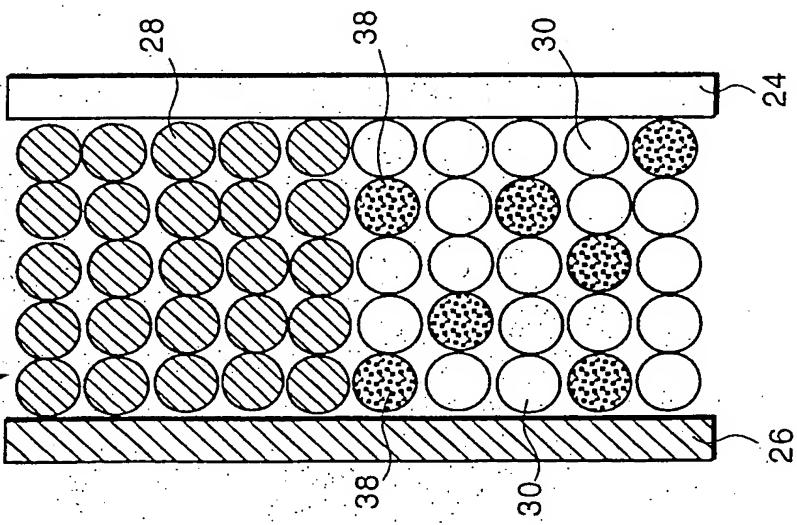
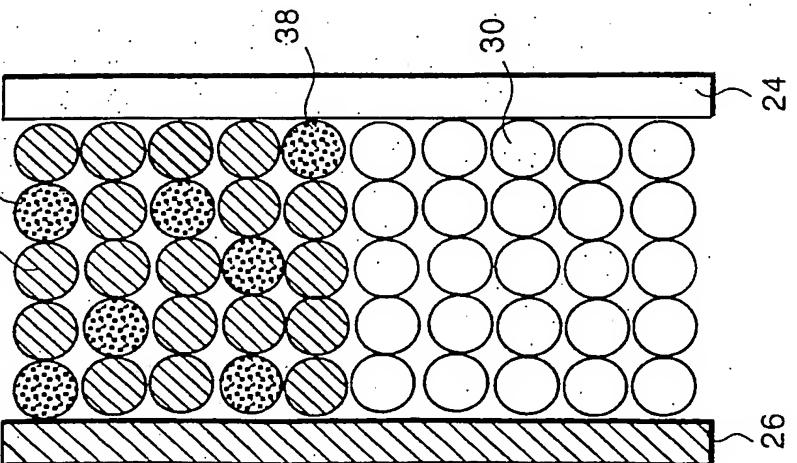


FIG. 1A

ANION
CATION
DOPANT



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FIG. 1D

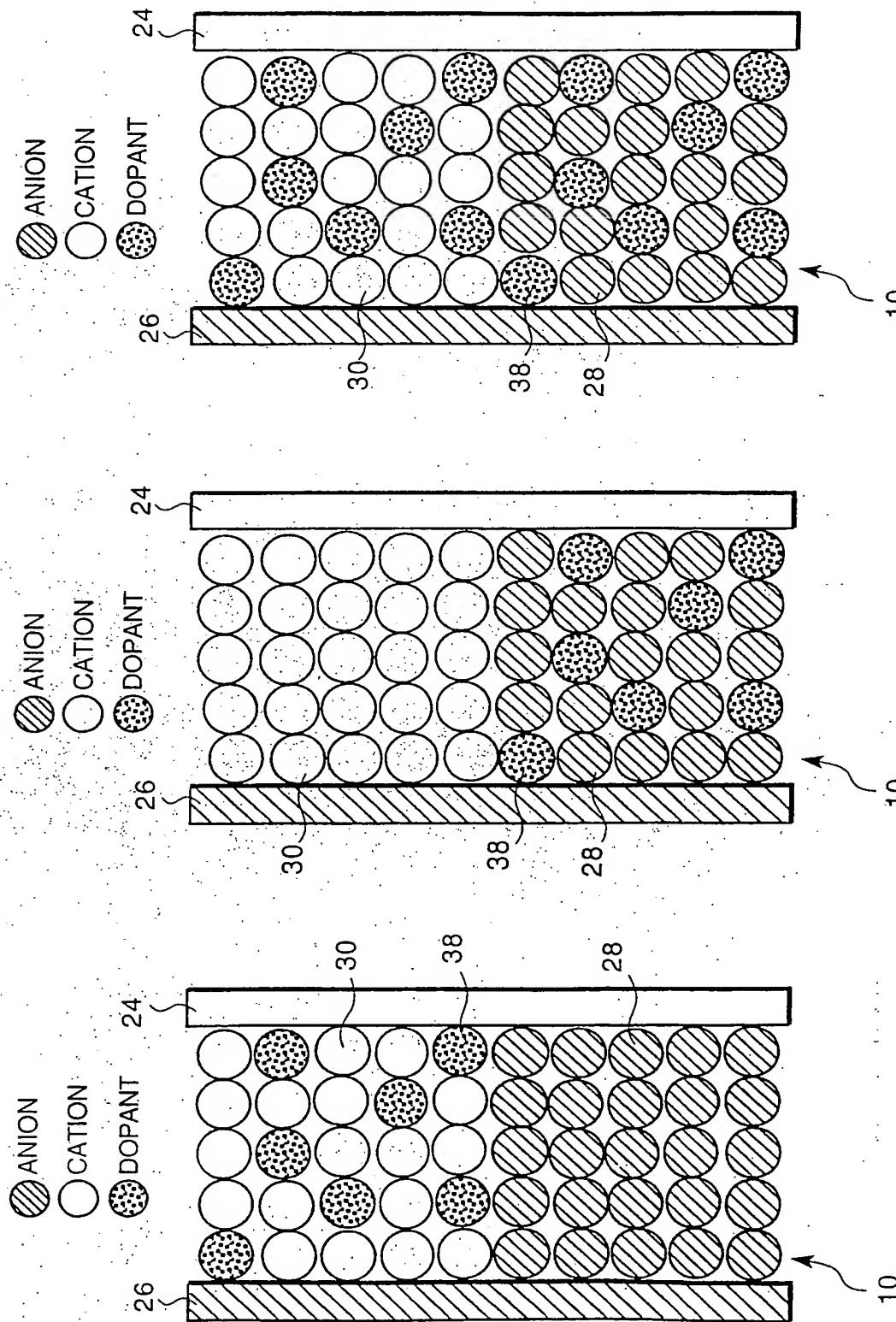


FIG. 1E

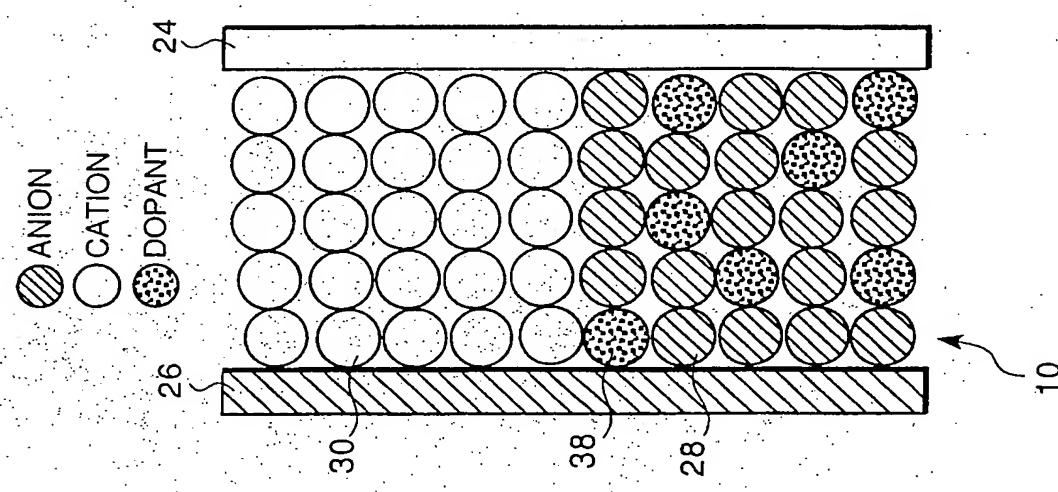
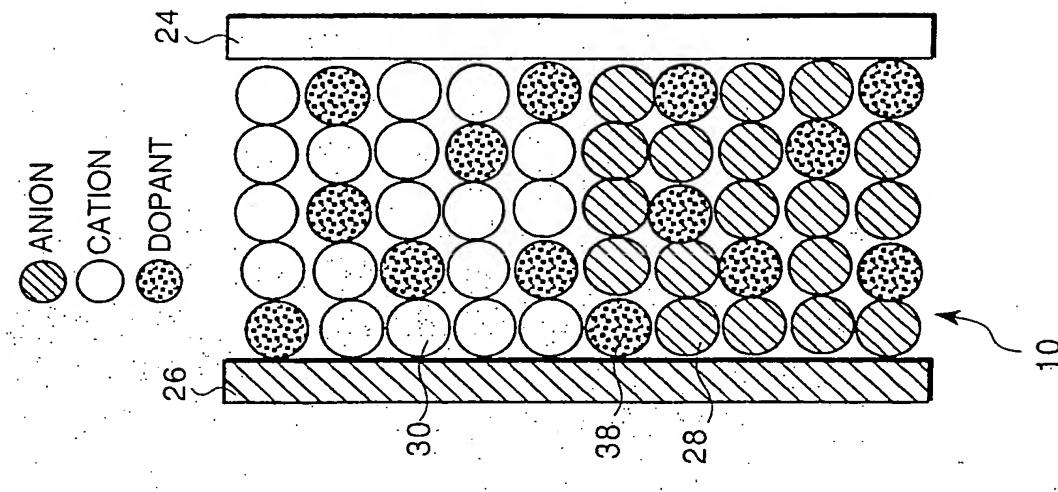


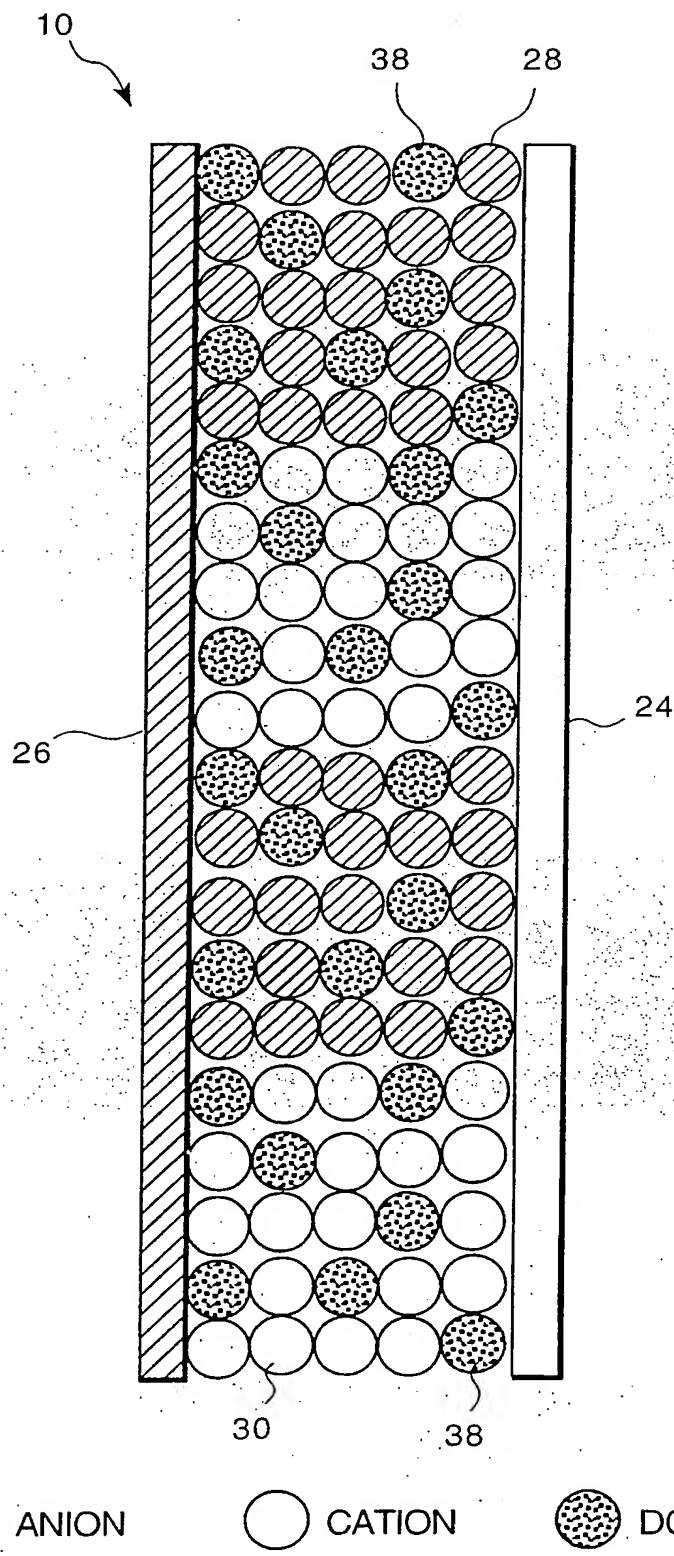
FIG. 1F



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FIG. 2



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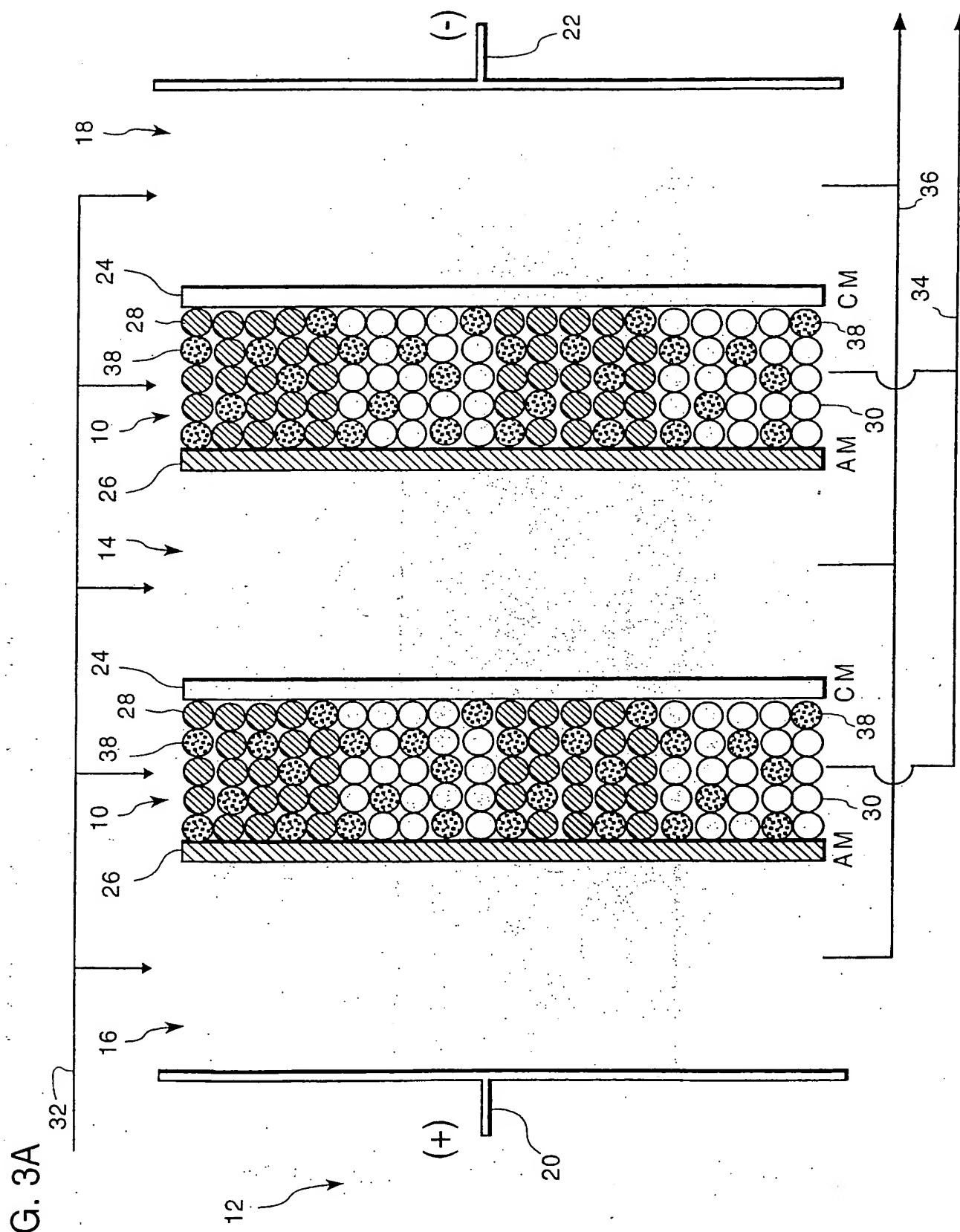


FIG. 3A

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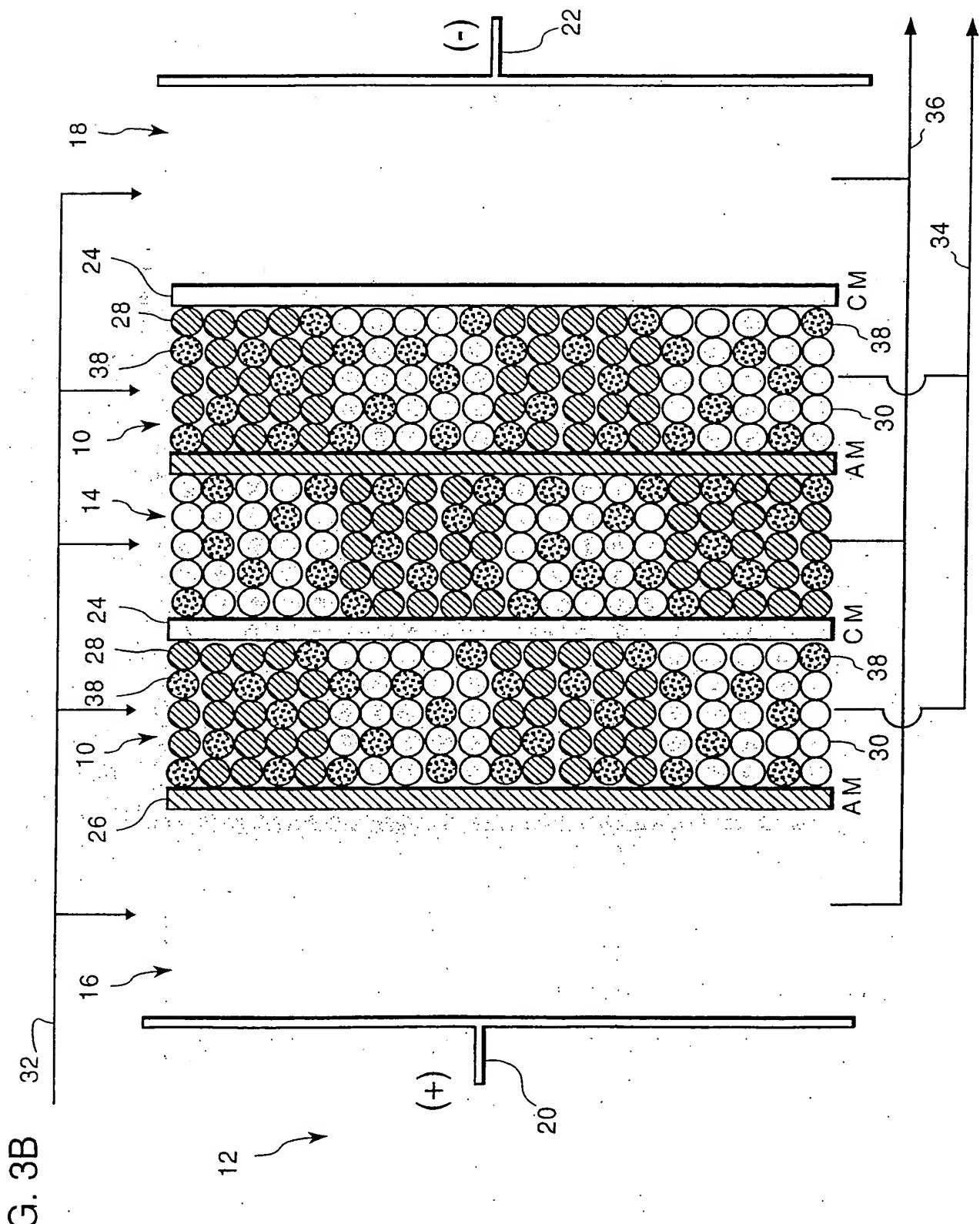
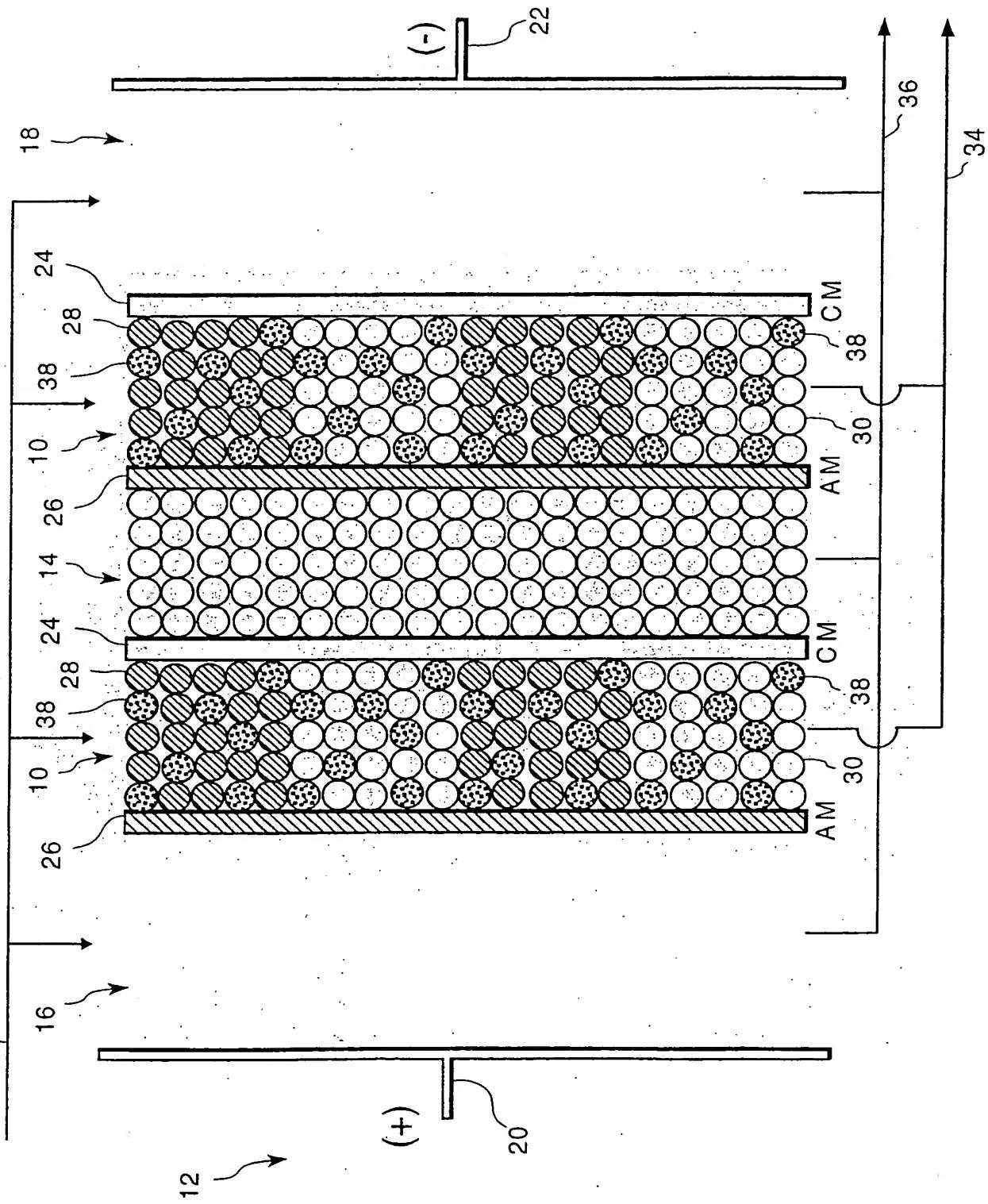


FIG. 3B

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FIG. 3C



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/01666

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B01D61/48 B01J47/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
 IPC 7 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|--|
| A | <p>WO 98 20972 A (UNITED STATES FILTER CORPORATION) 22 May 1998 (1998-05-22)</p> <p>page 5, line 19 - line 25; claims 1,2,7,18,26 page 9, line 15 - line 17 --- -/-</p> | <p>1-4,23, 24,41, 47,48, 59,60, 67, 75-79, 81,83</p> |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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